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# PHYSICO-CHEMICAL EVOLUTION

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# PREFACE

*IT is well known that since the investigations of Gibbs and Boltzmann, the principle of Carnot has assumed a new and unexpected significance, in the sense that the physico-chemical evolution of a system takes place towards states of greatest probability, equilibrium occurring when this probability is a maximum in the analytical sense of the term. The change of entropy which, in the language of thermodynamics, characterizes this evolution, will be proportional to the difference between the logarithms of the probabilities of the initial and final states.*

*Thus this new conception has introduced, with a particularly strong intensity, into the domain of physical chemistry the idea of the "statistical law," with all the consequences which it involves from the scientific and philosophical point of view.*

*By virtue of these conceptions the determinism of physico-chemical evolution appears, therefore, as a larger* statistical determinism, *in which the apparently inevitable exactness is only due to the law of large numbers. In fact, this determinism permits the occurrence of other very rare possibilities, or* fluctuations, *particularly when the law of large numbers is no longer entirely satisfied.*

*For this reason, the question of* absolute determinism *is transferred into the domain of the* individual

actions *between molecules, atoms, or electrons, which still evade our direct experimental investigations almost completely.*

*This seems to be a philosophical consequence of considerable importance.*

* * * * * *

*Three papers which deal with this problem and which have appeared during recent years, have been collected under the general title* Physico-Chemical Evolution. *These papers may be read independently, though relating more or less to the same subject.*

*The first, written and published in April,* 1918, *in the* Archives de Psychologie *of Geneva, in some way serves as an introduction. It is called "Reflections on the Classification and the Unification of the Sciences," and was written with the special object of showing how the principle of relativity is able to constitute a first step towards the union of sciences which are metaphysically separated by the conceptions on which they are founded, and the reader will do well to study it in this light. Hence, it is not absolutely coherent with the two papers which follow it, but it has the advantage of stating exactly the position of physics and chemistry among all the sciences and particularly with respect to the more general sciences of biology and psychology.*

*Thus the considerations which are developed in it appear to be of value for the more complete understanding of the two papers which succeed it; this has led to its reproduction.*

*We get to the root of the subject in the second paper, "The Evolution of Physico-chemical Phenomena and*

*the Calculus of Probabilities*" (Journal de Chimie physique, 1917, **15**, pp. 215–272).

*Its object is to show—as far as possible without the introduction of mathematical developments—the statistical significance of Carnot's principle, and how, with this new conception, the principle is found to be limited by fluctuations.*

*With the exception of a short digression on fluctuations in biological phenomena, and some remarks concerning the analogy, which can be rigorously established, between the so-called vital principle and Maxwell's demon, the paper is devoted exclusively to physico-chemical phenomena, such as are defined by the sole conceptions of number, space, time, and matter.*

*The last paper, "Carnot's Principle and the Physico-chemical Evolution of Living Organisms"* (Archives des Sc. phys. et nat., *May–June*, 1920) *goes further. It endeavours to show that Carnot's principle, considered as a statistical principle, must disappear when it is sought to apply it to more and more heterogeneous media, such as very probably constitute living matter, as the law of large numbers on which it rests then ceases to be applicable.*

*In this paper we have intentionally distinguished quite clearly between the point of view of classical thermodynamics and that of the new statistical conceptions; the conclusions which are to be drawn from the two points of view being diametrically opposite.*

*The last part of this paper is distinctly metaphysical; particularly the final paragraph, "Outline of a unicist philosophy based on Carnot's principle."*

*The reader, therefore, must not try to find in this*

*short review anything more than an example which we have endeavoured to adapt as much as possible to the present scientific ideas, but which is intended, above all, to bring forward the high philosophical importance of this idea of the statistical law.*

*By thus forcing itself always further and further into the domain of physical chemistry, this conception tends to thrust away into the unknown region of the atom or electron, or perhaps even beyond that, the exact nature of the first causes of the phenomena with which our "ego" is associated.*

GENEVA C. E. G.

# PHYSICO-CHEMICAL EVOLUTION

## EINSTEIN'S PRINCIPLE OF RELATIVITY IN ITS RELATION TO THE CLASSIFICATION OF THE SCIENCES[1]

### 1. *The progress of modern physics*

DURING the last thirty years modern physics has undergone changes much more complete and profound than had been recorded in the two centuries from the time of Newton to the appearance of the work of Maxwell.

In the first place, this science has continuously become more electromagnetic; that is to say, the phenomenon of electromagnetism has been considered more and more by physicists as one of the most general; the one which tends by appropriate simplifications or modifications to embrace all the others.

The first step in this direction was taken by Maxwell, to whom we are indebted, as is well known, for the electromagnetic theory of light, to-day

[1] This paper appeared under the title *Reflexions sur la classification et l'unification des sciences* (Archives de Psychologie, August, 1919, Geneva).

universally accepted by physicists. Since then, this tendency to explain physical phenomena by electromagnetic considerations has continually increased, and at the present time it even extends to mechanics, which previously appeared to be the unchangeable foundation of the older physics. Thus even the property of inertia which constitutes the fundamental postulate of classical mechanics has found a satisfactory explanation in the properties of the electromagnetic field.

In the second place, modern physics has become more and more a *granular and statistical physics*; that is to say, the conception of discontinuity which, in the atomic theory, already embraced all chemistry, has been extended into several other domains. Modern physics has had to have recourse to the atom of electricity (the electron), the actual existence of which is based on a very large number of experimental facts, and the numerical value of which has been determined by varied and already very exact measurements. Finally, this idea of discontinuity has not been solely limited to matter, but during the last few years it has invaded the domain of energy, which, accordingly, should be emitted by radiating bodies, not in a continuous manner, but in small discontinuous parcels, called "quanta."

One of the consequences of the discontinuity of matter is the importance which kinetic theories, that is, theories which consider the motions of these discontinuous elements, have assumed in physical explanations. Their starting-point was, as is well known, the kinetic theory of gases, to which

the laws of the Brownian movement have given an almost tangible confirmation. But to-day these kinetic theories are slowly invading the various domains of physical chemistry and the conception of "statical equilibrium" is being gradually replaced by the more probable conception of "dynamical equilibrium."

On the other hand, as the motions of these innumerable discontinuous elements (atoms, molecules, electrons) cannot be followed by the equations of dynamics, physicists have been compelled to have recourse, in the investigation of a large number of problems, to the calculus of probabilities. This has rendered inestimable service during the last few years by the control which it brings to the kinetic hypotheses, particularly in the domain of fluctuations.

One of the most important consequences of the prodigious number of discontinuous elements which is involved in the smallest phenomenon is the colossal number of the possibilities which may occur, with a more or less great probability that they will do so. Physicists have thus been led to modify, in many cases, the ideas which they had of the physico-chemical laws, that is, of the laws which govern a whole composed of an immense number of molecules. The evolution of a phenomenon tends to take place according to the greatest probability, and it follows that physico-chemical laws are viewed as statistical laws, very exact it is true, on account of the law of large numbers, but no longer possessing that character of absolute determinism and inflexi-

bility which it has been customary to attribute to them. It is in this way that the second principle of thermodynamics has assumed the character of a statistical principle of evolution since the researches of Gibbs and Boltzmann ; the evolution of a system always occurring "if not theoretically, at least practically" in the direction of a greater probability.

But among all the discoveries and advances of modern physics, the appearance of the *principle of relativity* is perhaps the scientific event which remains the most extraordinary and the most perplexing. This principle teaches us, in fact, that the ideas of time and space which we have held hitherto are only particular cases of a more general conception.

Whatever repugnance we may feel to renouncing our former conception of time and space, we are nevertheless compelled to recognize that the new principle allows a collection of phenomena, which had led to the multiplication of sometimes contradictory hypotheses, to be given a unique explanation. Further, by adopting the new point of view, the equations of the electromagnetic mechanics of very large velocities assume a form at once simple and general. Also, many brilliant minds and the best among actual physicists have not hesitated to regard the new conception as a more general and a more exact expression of the notions of time and space, although in practice the numerical difference between the two conceptions is only appreciable in a very small number of cases.

Others have sought and still seek to avoid such a far-reaching transformation of our mode of thinking; they hope that we shall succeed in finding a satisfactory explanation of the collection of facts which have justified the appearance of the new principle without forsaking the old conceptions.

At the present time it is not possible to say which of these two schools of thought will eventually triumph. But it has seemed of interest to bring forward in this communication what would be, particularly from the point of view of the classification and the unification of the sciences, the modifications involved by this *correlation between the measurement of time and that of space which is the very foundation of the principle of relativity.*

It is this point of view therefore which will be exclusively adopted in what follows.

### 2. *The comparison of lengths and of intervals of time in relativity* [1]

From the experimental standpoint the principle of relativity can be expressed as follows:

*The laws which govern physical phenomena are independent of a uniform translatory motion in which the observer and all the material bodies concerned are involved.*

This conclusion, which has been verified by ex-

[1] For a more complete investigation of these questions we would refer the reader to the articles which have already appeared on this subject, particularly to the very clear exposition which Langevin has given in the review "Scientia," under the title *L'évolution du temps et de l'espace* (1911).

periment with a very high degree of accuracy, was difficult to reconcile with the hypothesis of an immobile ether in which luminous waves, or more generally electromagnetic waves, were propagated with a constant velocity. From this difficulty was born the principle of relativity, summarized by the Lorentz transformation and the kinematic equations of Einstein.

Among the numerous consequences which result from these equations we shall confine ourselves to recalling two only, which are particularly perplexing ; they will be sufficient for our purpose.

The expression of a length is given by the relation

$$d' = d\sqrt{1-\left(\frac{v}{V}\right)^2} \qquad (1)$$

in which $d$ might be, for example, the length of a rule to an observer motionless with respect to it—that is, the length which we consider in ordinary dynamics—whilst $d'$ would be the expression for the length of the rule to an observer moving with a uniform relative velocity $v$ parallel to it ; finally $V$ is the enormous velocity of light, so that the term $\left(\frac{v}{V}\right)^2$ is practically, if not entirely negligible, at least always extremely small. The difference between $d$ and $d'$ is therefore inappreciable.

Similarly the expression for an interval of time is

$$\Delta t' = \frac{\Delta t}{\sqrt{1-\left(\frac{v}{V}\right)^2}} \qquad (2)$$

in which $\Delta t$ might be, for example, the expression for the interval between the ticks of a clock as heard by an observer belonging to a system A; $\Delta t'$ would be the expression for this interval as heard by the same observer if an *identical* clock, stationed for example on system B, moved with a uniform velocity $v$ with respect to him.

In short, the formulæ (1) and (2) show:

(1) That the expression for a length depends not only on the conception of space but on that of time also, since it involves the relative velocity $v$ of the two systems;

(2) That the expression for an interval of time, for the same reason, depends not only on the conception of time but also on that of space.

It follows that in relativity the conceptions of space and time are inseparable from each other. It is only when the relative velocity $v$ of the two systems is small with respect to that of light that the two conceptions become independent and that the formulæ (1) and (2) reduce to

$$d' = d, \quad \Delta t' = \Delta t,$$

corresponding to the ideas of space and time which are usually held.

### 3. *The classification of the sciences and the principle of relativity*

From the philosophical point of view there can only be one science: "Science," which must embrace the explanation of all phenomena, whatever they may be, with which our "ego" is associated.

But we are so far from being able to realize this ideal synthesis—even if it is realizable—that because of our inability we have subdivided the whole of our knowledge into a certain number of arbitrarily established categories.

It is not useless to recall this truth, though it is so commonplace; it is because we do not possess "Science" that we have "sciences."

Among the numerous modes of subdivision there is one which we shall call here the *metaphysical classification* and which is based on the primordial conceptions of *number*, *space*, *time*, *matter*, *life*, and *thought*; each of which conceptions is in reality for us an enigma, a profound mystery.

The definition which can be given to each of these fundamental conceptions, the study of their origin and of the relations which may exist between them belongs, or at least approaches very closely, to "Metaphysics"; we shall not dwell on them at present.

Nevertheless, it may be questioned whether these conceptions will always be puzzling to us or whether some day, by patience and work, we shall be able to penetrate to their deepest meaning, to the mystery which they conceal, or at least to the relations which unite them. Are these conceptions really irreducible or will they some day throw light on one another? Finally, is it possible that they are derived perhaps from one and the same principle which we cannot at present perceive?

METAPHYSICAL CLASSIFICATION [1]

| | Number. | Space. | Time. | Matter. | Life. | Thought |
|---|---|---|---|---|---|---|
| Arithmetic | × | | | | | |
| Geometry | × | × | | | | |
| Kinematics | × | × | × | | | |
| Mechanics, Physics, Chemistry, Astronomy | × | × | × | × | | |
| Biology | × | × | × | × | × | |
| Psychology | × | × | × | × | × | × |

In this connection the *principle of relativity* deserves our attention for a few moments.

As we have just seen, this principle rests essentially on a correlation between the measurement of time and that of space, which become to some extent inseparable from one another.

This correlation has the inestimable advantage of introducing simplifications of the highest importance into the explanations of physical phenomena. In the first place, it allows the mechanics and the physics of bodies in motion to be considerably simplified in the case of very large velocities; further, it tends to reduce to a unique principle the two

[1] It may be observed that the order in which the various sciences occur is identically that of the classification (theorematic) of Professor Adrien Naville, *Nouvelle classification des sciences*, 2nd edition, 1901, Félix Alcan, Paris. If we have thought it best to call this classification the *metaphysical classification*, it is with the object of bringing out the profoundly enigmatical character of the fundamental conceptions on which they are founded.

principles which are perhaps the most important and the most firmly established in modern physics: "the conservation of mass and the conservation of energy." Thanks to this supposed relation between time and space, every body only possesses inertia or even weight in proportion to the total energy which it possesses: inertia and energy thus become, so to speak, synonymous. Moreover, the new principle allows the almost complete elimination, in the explanation of phenomena hitherto observed, of that hypothetical medium of reference the ether—to which physicists have accustomed us and the properties of which have had to be multiplied in order to explain various phenomena; the general solution of these phenomena seems to have been accomplished by the principle of relativity.

It is therefore incontestable that *the introduction of the new principle, revolutionary as it appears, constitutes an important element of unity between the various domains.*

But the adoption of a conception which has the effect of revolutionizing ideas which are as familiar to us as those of time and space must occasion repugnance and very active opposition.

Its opponents have said, "We are willing to admit that the formulæ of relativity contain some profound truth since they lead to results which hitherto have been in accord with experience, but let us seek another interpretation and please do not let us modify the conceptions which for us possess axiomatic evidence."

To this the partisans of the new principle can

reply, not without reason: "We do not overthrow the conceptions of time and space, we generalize them. These conceptions in fact are only inseparable from one another in the case where the relative velocities of the bodies are enormous. As soon as these velocities are small with respect to the enormous velocity of light, the conceptions of time and space again become practically independent of each other.

"But this last case is precisely that of the world in which we are placed. It is not surprising, therefore, that the independence of these two conceptions appears to us to be axiomatic. If we could live in a world where the relative velocities of material bodies approached that of light, it is to be presumed that our conceptions of time and space would be different, that these two conceptions would become connected and that in order to explain the dynamics of these enormous velocities we should be led precisely to the equations of relativity.

"Thus it is because we live in a world which is only a particular case of a more general universe that the conceptions of time and space appear to us to be independent of each other. In the world of the radioactive atom which emits electrons the velocity of which approaches that of light this would very probably not be the case."

Considered from this point of view it is seen that the principle of relativity is above all a *metaphysical acquisition.* Perhaps the principle of generalized relativity recently advanced by Einstein may be a new step forward in that path of metaphysical

progress which some day may be able to inter-relate the diverse fundamental conceptions which are at the bottom of our classification of the sciences.

### 4. *Note on the origin of the fundamental conceptions of the classification of the sciences*

Since our various sciences have been artificially separated from one another by the number of fundamental conceptions which they involve (see the table, page 9), perhaps it will be profitable, without dwelling at length on their definition, to say a few words concerning each of them, in order to recall how they are connected with the sensations with which we are familiar; that is, their connection with the "particular case" in which we exist. This rapid review will have the advantage of bringing out clearly to what extent convention is at the base even of the conceptions on which our classification of the sciences rests.

The conception of NUMBER would appear to have *discontinuity* for its origin, whatever the manner in which this discontinuity manifests itself to our senses: form, colour, sound, touch, and so on.

The conception of SPACE and of its measurement would appear to be connected with that of *a solid body gratuitously supposed to be invariable whatever the position it occupies, its orientation, or its velocity*; similarly, *the equality of two spaces supposes the superposition of two solids, "invariable by definition."* But we have just seen (§ 2) that the principle of

relativity has the effect of modifying this original conception and that the magnitude of a length depends on the relative velocity between the observer and the length to be measured.

The conception of TIME would appear to be intimately connected with that of *variation.* In fact it is not possible from the physical point of view to imagine that any conception of time could exist in a universe in which everything was at rest, and in which no variation whatever occurred. For that universe time would not exist ; at least nothing would permit of its measurement.[1] *The equality of two intervals of time thus arises from the supposition that " the same causes take the same time to produce the same variation."* The conception of the simultaneity of two events is more difficult to define ; it also rests on conventions very clearly stated in particular by H. Poincaré.[2] We shall excuse ourselves from dwelling on these difficult questions here, and we shall content ourselves with remembering that the principle of relativity has profoundly modified these conceptions, as it has done those of space.

The conception of MATTER would appear to have for its origin the resistance which bodies offer to

[1] Of course, only physical time is here concerned and not time such as may be considered in psychology—Bergsonian time, for example.

[2] H. Poincaré, *L'espace et le temps* (Dernières Pensées) ; *La relativité de l'espace* (Science et Méthode) ; *La mesure du temps, la notion d'espace* (La Valeur de la Science).

muscular effort, when it is endeavoured to displace them or, more generally, to modify their motion. From this point of view inertia is the property which seems above all to characterize matter. But here again the principle of relativity intervenes to attribute inertia in a general way to the energy which a body possesses. It follows that "energy" and "matter" are only the two aspects of one and the same thing; and it can be better understood thereby why force and matter are always inseparable from one another.

To sum up: the principle of relativity tends to modify profoundly the conventions which are at the base of our habitual conceptions of space, time, and even of matter, conventions which are principally justified, it appears, because hitherto we have not had to take into consideration material bodies possessed of velocities sufficiently large with respect to that of light.

It is not easy to define briefly the conception of LIFE; it embraces, indeed, quite a collection of facts which appear common to all the organisms which it has been thought necessary to call "living" on account of the very existence of these facts.

Let us only recall that the living being is characterized by the fact that it is born, grows, reproduces, and dies; that its growth is a growth which is generally different for the various organs, this being contrary to what occurs in crystals which also are born, grow and die, but of which each part, however

small it may be, is only the repetition of any part whatever of the whole. The primordial element of the development of the living being appears to be probably the cell; but this cell varies and develops according to the organs which it is its mission to constitute or to renew. As is well known, the living organism has the faculty of increasing at the expense of the materials which are to be found in the surrounding medium; but above all it has the faculty of choosing from among these substances those which are appropriate to its development or to its functioning, and rejecting those which are useless or harmful to it, though the physico-chemical process of this assimilation, etc., is not yet satisfactorily explained.

But above all these properties, the generality of which could, I think, be disputed in many cases there is an experimental fact which overshadows all the other facts: *life only appears to proceed from life itself.* As Bergson has said, "life would appear to be like a current which goes from germ to germ by the intermediary of a developed organism," and it must be recognized that the impossibility of practically realizing the spontaneous generation of life provides this point of view with an experimental argument of the first order.

Will it always be thus? Obviously we cannot say, but meanwhile this practical impossibility of creating life, otherwise than by life itself, fully justifies the classification of vital phenomena in a separate category, at least provisionally.

As for the conception of THOUGHT, it seems desirable entirely to give up hope of defining it ; it is the mystery of mysteries. Probably all that science can teach us positively in this direction are the correlations which unite it to the biological and physico-chemical phenomena *which, experimentally, always accompany it* ; and even this is much to require of it.

In conclusion, it is seen from what has been said that the fundamental conceptions which have served to separate our various sciences from each other rest on conventions the choice of which appears to be connected with the special conditions of the world in which we live. But it may be desirable to modify these conventions, and it even seems as though this had been accomplished for the conceptions of space, time, and matter by the introduction of the principle of relativity.

It would appear that in this there is a first step in that advance towards "Science" which must establish in this way relations between these diverse metaphysical conceptions which appear to us at first sight to be irreducible, but which the principle of relativity seems to have revealed as being more unified than we thought, at least as far as space and time are concerned.

What progress can be realized in the future in this direction ? In particular, is it permissible to hope some day to be able to establish a correlation between physical chemistry and life, between life and thought, and so on ? These are very big

questions, to which nobody can reply in the present state of science.

Nevertheless, we think it well to recall in this connection an ingenious hypothesis which endeavours to make Carnot's principle the line of demarcation between physico-chemical phenomena and vital phenomena. This hypothesis has been fortunate enough to have the illustrious physicist Helmholtz as its first sponsor. Perhaps we shall some day return to this hypothesis to present it in a form more adequate to the conceptions of modern physics. For the time being, however, we shall confine ourselves to some considerations of the degree of generality of the various sciences in our table.

### 5. *Considerations of the degree of generality of the various sciences*

Speaking generally, how can we hope to pass from the sciences to "Science"? In other words, what path must we take in the endeavour to interrelate the metaphysical conceptions which separate the various sciences of our classification?

As is well known, it is scarcely possible, in the present state of our knowledge, to reply to such a question. Also, we shall confine ourselves, in what follows, to giving some vague indications which result, above all, from the *degree of generality which we have assigned to our various sciences.*

Of all the phenomena with which our "ego" is associated, the most general and that which overshadows all and embraces all is thought.

There is, in fact, no thought which has not experimentally a living organism for substratum; there is no living organism which is not the seat of physico-chemical phenomena; and finally there is no physico-chemical phenomenon which does not involve the conception of number, space, time, and matter.

Thus thought embraces all the metaphysical conceptions which are at the base of our classification of the sciences; from our point of view it is the most general phenomenon.

EXPERIMENTAL PSYCHOLOGY in its largest sense should therefore study simultaneously with the psychical phenomenon all the physiological and physico-chemical phenomena which accompany it. It is scarcely necessary to say, however, that such a study is so vast, entails such varied and profound attainments, and encounters so many actually insurmountable difficulties that no psychologist dare undertake it even in the simplest cases.[1]

[1] Nevertheless, the hope may be expressed that one day some experiment of this nature may be partially attempted; but this can only be after the other sciences have been carried to a degree of perfection which at present they are far from attaining.

In this connection may be mentioned the experiments in which it has been shown that a man placed in a calorimetric chamber does not liberate more heat when he is engaged in hard mathematical work than when his brain is, so to speak, inactive. This negative conclusion does not appear to us to be final, in view of the low sensitivity

Be that as it may, the impossibility which the psychologist finds in studying completely the problems which interest him has the effect in practice of making psychology into an artificially simplified science, although in principle it is the most general of all.

After experimental psychology comes BIOLOGY, which can also be called PHYSIOLOGY if all psychical considerations are deliberately excluded,[1] as we do in our classification, and as is done practically in the majority of biological investigations. This exclusion, which is manifestly arbitrary in the case of the animal kingdom, may appear to be justifiable where plants are concerned. In fact a plant appears to possess neither brain nor nervous system; nevertheless, certain facts seem to indicate that it has a rudimentary intelligence; these facts authorize us not to consider the psychism of a plant or even of a cell as definitely settled in the negative. Do we not see, in fact, certain plants turning themselves towards the light; the tendrils of climbing plants seeking and finding their support, the drosera closing at the contact of an object and imprisoning in this way the insect which is its food, and so on? It is true that the biologist may very well regard these

of such an experiment; the large amount of heat liberated by the rest of the body must be added to that set free by the brain in both the comparative experiments.

[1] M. Adrien Naville defines biology as follows: "The science of the laws of corporal life." It is considered here in the same sense.

facts as only signs, perhaps encouraged in this way of looking at them by the preconceived idea that some day physico-chemical phenomena, which have all his confidence, will furnish the explanation of life, considered thus gratuitously as a physico-chemical climax.

It would be arbitrary therefore to suppose *a priori* that a plant is deprived of all sensibility and of all psychism.

It follows that *biology* also is found to be *an artificially simplified science*, above all so far as it concerns the animal kingdom, and in particular the higher animals.

After biology we have on our table (page 9) mechanics, physics, chemistry, and astronomy, which we shall designate here by the single term PHYSICAL CHEMISTRY.[1] The postulates and the fundamental laws of physics and chemistry may all be said to have been established by experiments or by observations made on non-living matter. We do not owe them to the chemistry of plants or animals or even to the chemistry of ferments, in spite of the immense interest which the latter study presents. They result, above all, from experiments made, if not on substances or media which are absolutely sterile, at least under conditions where the influence of vital or psychical phenomena was apparently and

[1] This term is given a more general meaning than it usually possesses; by the term physical chemistry is meant all physical and chemical phenomena, between which there is moreover a very subtle distinction.

probably nil. It is for this reason that *physical chemistry in its turn must be considered to be a simplified science* as it involves only the conceptions of number, space, time and matter. It will constitute a complete science only when its relations with vital and psychical phenomena are known.

After physical chemistry come two sciences the artificial simplicity of which is so obvious that it is unnecessary to insist on it. They are KINEMATICS, which studies the motion of bodies, but arbitrarily eliminates the properties of the matter which constitutes them ; it thus involves the conceptions of number, space, and time ; finally GEOMETRY, which studies the properties of figures traced out in space, but without involving time. To a geometrician, a figure can be developed by the displacement of another figure, but the time which this displacement has occupied does not enter into consideration ; geometry can only involve the conceptions of number and space.

Nevertheless it is important to observe that the principle of relativity tends to reunite kinematics and geometry in the same metaphysical category, since the conceptions of time and space are thereby unified. Our Euclidian geometry would then be only a particular case ; it would be a geometry in which the dimensions of the figures would be always measured by means of rulers motionless with respect to them.

In the last place comes ARITHMETIC, which is

metaphysically the most simplified of all the sciences.

An example will be given to bring out more clearly the degree of generality of the various sciences in our classification.

Consider a geometrical figure—a parabola ; this figure can correspond to an infinite number of kinematical problems. The parabola in question may, in fact, be described by a particle moving according to laws of motion which may be varied in an infinite manner.

Let us consider now a parabola described by a particle moving "according to a given law" ; an infinite number of physical problems can correspond to this exact kinematical problem. For example, it might be the problem of a ball of lead projected with a certain initial velocity and at a particular angle in a gravitational field ; but it might equally be that of an electron projected at the same angle in a constant electric field, and so on.

It is seen, therefore, that a particular geometrical problem can give rise to an infinite number of kinematical problems, and that an infinite number of physical problems can correspond to a particular kinematical problem.

Similarly it may not be impossible that an infinite number of different psychical phenomena correspond to a given physico-chemical phenomenon occurring in the brain of a living being. It will be understood that here we enter into the region of dreams ; the reader will pardon us if we digress for a little ; it will permit us to state our ideas more precisely.

*Note* 1.—Let us first recall that a physico-chemical law, or more generally a physico-chemical phenomenon, may be considered as a statistical result. When we have before us two cubic centimetres of the same gas, each enclosed in a separate receptacle and both brought to the same temperature of 0° C. and to the same pressure of 760 mm., we say that these two cubic centimetres of gas constitute the same phenomenon from the physico-chemical point of view. But actually if we were able to examine the complexity of their molecular movements we should state that the phenomenon which we call a cubic centimetre of gas at 0° and 760 mm. can correspond to an infinite number of different distributions of velocities or of positions of the molecules. Thus from this point of view no two cubic centimetres of gas can be considered as identical.

Let us suppose that the methods of investigation will some day permit us to be cognisant of this diversity, partially at least—and we must not quite give up hope of this since on the one hand X-rays have already given us information concerning the arrangements of the molecular networks in crystalline systems, and on the other hand the study of the fluctuations enables us to penetrate into the heart of the physico-chemical laws. Let us suppose therefore that we should then be able to establish that each of these dispositions, although they are practically equivalent from the physico-chemical (i.e. the statistical) point of view, corresponds to a definite psychical phenomenon. We shall then be able to understand why physico-chemical and psychical phenomena do appear and must appear to us to be metaphysically distinct. In other words, while we confine ourselves to considering in physico-chemical phenomena only the statistical result of the whole, this only being accessible to our determinations, no precise correlation between thought and matter can appear, although experimentally thought is always associated with matter. But by penetrating more deeply into the heart of physico-chemical phenomena we may have some

chance of laying hold of this correlation, in the same way as the experimental investigation of the mechanics of high velocities with electrons has led to the establishment, by the principle of relativity, of a correlation between the measurement of space and that of time. From this example it is apparent how the simultaneous study of a psychical phenomenon and of the physico-chemical phenomenon which accompanies it may help us to understand more clearly the significance of the physico-chemical phenomenon itself; just as we grasp more thoroughly the true meaning of inertia in Newtonian mechanics by considering this science as a particular case of electromagnetism and of the more general mechanics of relativity.

Finally, if we have thought it necessary to emphasize, in a way which may seem rather excessive, *the voluntarily and arbitrarily simplified character of our various sciences*, it is in order to avoid the risk of falling into too hasty generalizations. As a celebrated mathematician has said: "One never obtains from an equation anything except what has been put into it"; whatever may be the permissible transformations to which it is subjected the final result was always contained in the original equation. Similarly, nothing can be obtained from an artificially simplified science which is not contained in its postulates.

* * * * * *

In conclusion, we have just seen that our diverse sciences, which we have classified and defined, are separated from one another by the larger or smaller number of the metaphysical conceptions which

they involve ; and, in the second place, we have insisted on the degree of generality and on the voluntarily and arbitrarily simplified character of every one of these sciences.

This done, we have said that the advance towards "Science" must tend to establish relations "based on experience" between these various metaphysical conceptions which appear to us at first sight to be irreducible, but which the principle of relativity has recently revealed to us as being more related than we thought, at least so far as space and time are concerned.

But, in this metaphysical conquest, which alone can lead us to the desired goal, what path are we to choose ? We shall endeavour to ascertain this from the history of the experimental sciences.

This teaches us, in fact, that in order to establish relations between two phenomena we have two principal methods of procedure at our disposal. We can either complicate the phenomenon which appears to us to be the simpler or we can simplify that which appears to be the more general. In other words, we can proceed from the particular to the general or we can follow the reverse order and go from the general to the particular.

Let us suppose, for example, that we wish to establish a relation between physico-chemical phenomena as we know them and vital phenomena ; we may then try to complicate the physico-chemical phenomenon, which appears to us to be the simpler, in such a way as to make it include the vital phenomenon ; or inversely, we may try to simplify the

vital phenomenon so that we get back to the laws of our physical chemistry.

But these two ways are far from offering theoretically the same security, and above all from presenting the same difficulty. In order to simplify a phenomenon it is only possible to act on a limited number of elements. It would appear that by successive simplifications it should be possible to recognize fairly quickly whether the second phenomenon was contained in the first, and vice versa. But in order to complicate a phenomenon and to make it more general, the choice of complication is in some ways unlimited, since new elements can always be added. The difficulty of choosing may then become so great as to render it absolutely impossible.

Thus physicists have been able to arrive at a satisfactory and more general explanation of luminous phenomena by starting from electromagnetic considerations, whilst it would have been nearly impossible for them to explain electromagnetism merely by the mechanical considerations which were at the bottom of the old theory of light. This difference arises from the fact that light is only a particular case of electromagnetism; it was therefore possible to explain light by simplifying electromagnetism, whilst it is very difficult to say how the mechanical theory of light can be complicated in order to embrace electromagnetism. Moreover, all the efforts which physicists have made to give a satisfactory mechanical explanation of electromagnetic phenomena have been in vain, though

by starting from electromagnetic considerations they have been able to create a satisfactory image of inertia and even to furnish a kind of explanation of mechanics.

Similarly, it is easier to give an account of Newtonian mechanics by taking as a starting-point the more general mechanics of relativity, applicable to the enormous velocities which the cathode electrons or the $\beta$ rays may possess, than it is to start from Newtonian mechanics, established with velocities small with respect to that of light, and to endeavour to deduce therefrom the dynamics of these enormous velocities.

Therefore, although this conclusion may not be at all general, it appears to be easier to explain a particular phenomenon by commencing with a more general phenomenon, which is simplified, than to adopt the reverse process. Similarly, in order to understand more clearly the meaning of one of the sciences of our classification it is perhaps necessary to consider it as a limiting case of a science which is metaphysically more general. In other words, *we shall only understand completely the meaning of a physico-chemical phenomenon when the relation is known which unites it to the vital and psychical phenomena which can accompany it in the living organism.*

*In short, is it not by the study of physico-chemical phenomena that we have been led to the discovery of the principle of relativity and brought at the same time to understand kinematics and geometry in a more complete and much more general way?* It is there-

fore indeed by the study of a science which is metaphysically more general (involving the conceptions of number, space, time, and *matter*) that we have been able to generalize two sciences which only involve a smaller number of these fundamental metaphysical conceptions.

Thus it appears theoretically more rational to proceed from the general to the particular and to explain one science by a metaphysically more general science than to follow the reverse order.

This is not the case in practice, and we know that on account of the inextricable difficulties which are presented by the simultaneous study of psychical phenomena and of the concomitant physico-chemical phenomena, our individual sciences must be studied by themselves for a long time yet without our being greatly concerned with the relations which may exist between them.

In this connection, let us remember that optics and electromagnetism could never have been welded into a single theoretical whole if Huyghens and Fresnel on the one hand and Faraday and Maxwell on the other had not brought each of these sciences to a very high degree of perfection.

Similarly, it has been possible to give an experimental basis to the principle of relativity, and thus to achieve progress in metaphysics by means of physics itself, by increasing the precision of experimental methods, and particularly of interference methods, and of electromagnetic measurements.

Thus the advance towards "Science" can only

be very slow. But the very perplexing discoveries of modern physics, and particularly that of relativity, give us some gleams of hope that we shall some day see science become that general synthesis which has at all times been its ideal. Unfortunately, these gleams are still very feeble; they cannot blind us to the extent of hiding from us the immensity of the distance we have to travel.

# THE EVOLUTION OF PHYSICO-CHEMICAL PHENOMENA AND THE CALCULUS OF PROBABILITIES [1]

## INTRODUCTION

If one is sufficiently lavish with time, everything possible happens.

HERODOTUS.[2]

AS you know, physicists and chemists usually consider the second principle of thermo-dynamics (the Carnot-Clausius principle) as a kind of principle of evolution in the domain of physico-chemical phenomena ; in the sense that the

[1] Lecture before the Société de Physique et d'Histoire naturelle de Genève, December 7, 1916.

This lecture was delivered before an audience in which physical chemists were in a minority ; readers will be good enough to forgive the repetition, occasionally in some detail, of the elementary conceptions with which they may be familiar. It has been thought best to retain this essay in its simple form, only adding some developments ; the purpose of the essay being principally to bring out the inner meaning of the actual interpretations of the second principle of thermo-dynamics.

[2] This thought of Herodotus has been put in this form by F. Amiel, *Jour à Jour*, Paris, 1880 ; I am indebted to my late colleague and friend, Prof. Cailler, for bringing it to my notice.

evolution of an isolated system is always accompanied by an increase in its entropy.

But since the researches of Gibbs and Boltzmann this principle has received a particularly interesting and suggestive interpretation. From this new point of view it appears that physico-chemical phenomena have the effect of causing a system to evolve towards states which are more and more probable.

It thus happens that the calculus of probabilities creates a disturbance, in a quite unexpected manner, in a domain where it seemed that the most absolute determinism must always reign supreme.

You will permit me, therefore, by way of introduction, to recall briefly how the calculus of probabilities has little by little intervened in the explanation of physical phenomena and why it daily assumes a more important place.

## 1. The discontinuous structure of matter and the kinetic theories

Although the senses of sight and of touch are sometimes able to make us believe that matter possesses a continuous structure, the study of physico-chemical phenomena leads us more and more to assume that this structure is in reality discontinuous, "granular," as it is the tendency to call it to-day.

This discontinuous structure is asserted in the first place by all chemistry.

It would appear to be very difficult to explain without it, in an equally simple manner, the fundamental laws of definite and of multiple proportions which are the foundations of the atomic theory.

In the domain of physics this discontinuity is again found at every step, particularly in the kinetic theories, of which the Basle scientist, Daniel Bernoulli, had the immortal glory of laying the first scientific foundations.

For some years past the remarkable experiments made on the Brownian movement have given to these kinetic theories a reality which they had not previously possessed. These experiments have thrown a visible bridge between these theoretical conceptions, which were of the nature of hypotheses, and the reality of the movements of the particles which are directly accessible to observation. It will be sufficient to recall that the experiments of Perrin on the Brownian movement have permitted the redetermination of some of the principal constants of the kinetic theory of gases, to a very close approximation.

But this conception of the discontinuity of matter has not been confined to the individual particles, molecules or atoms; it has been extended to the domain of electricity, and we have witnessed the appearance of the electron, or atom of negative electricity, the existence of which is now supported by a large number of facts and more particularly by the experiments of Millikan, who more than any other has brought out the granular structure of the

elementary electric charge.[1] Moreover, this conception of discontinuity is not confined solely to matter; we see it introduced also into the domain of energy with the very fertile hypothesis of quanta, without which the experimental laws of luminous radiations appear to be difficult to explain.

Let us recall, in fact, that according to this hypothesis the emission of radiant energy only occurs in small parcels (quanta), having something of the nature of grains of energy.[2]

But though physicists increasingly assert the discontinuity of matter they do not less frequently continue to argue and above all to calculate as if it were continuous.

A problem will sometimes be discussed from both these points of view. Such a problem, for example, is the propagation of heat by conduction, which may be investigated either by assuming the point of view of continuity and starting from Fourier's differential equation or by adopting the kinetic

[1] In this connection see Schidlof and A. Targonski, *Arch. de Genève*, 1916.

[2] It is interesting to recall how nearly this hypothesis of quanta takes us back in certain respects to the classical theory of emission. It follows, in fact, from the principle of relativity (Einstein) that energy should possess a certain inertia. A body which radiates energy should thus theoretically lose a little of its inertia. The quanta which escape would be the vehicles of this inertia and should possess therefore the property characteristic par excellence of matter. In addition, from this point of view inertia and energy are scarcely separable. (On this subject see Langevin, *Inertie de l'Energie*, Journal de Physique, 1913.)

theory of electronic conductivity, which is more complex but which penetrates more deeply to the essentials of the phenomena.

The first method of calculation is in general simpler, and if it is only necessary to consider the phenomenon as a whole it leads to the same results. Why, then, should it cease to be applied in all the cases in which it has been shown to be sufficient? Physicists and chemists are bound to use all the means at their disposal to arrive at the knowledge of the truth, i.e. the relative truth.

## 2. The introduction of the calculus of probabilities into physico-chemical theories

One of the most important consequences of this discontinuous structure of matter is the large number of molecular or atomic elements which are concerned in the smallest phenomenon, in the smallest experiment. It follows that if it is desired to calculate "in a complete manner" even the simplest phenomenon, insurmountable difficulties are encountered from the very first.

Physicists, blinded by the success of the astronomers, tried, indeed, at first, to create a molecular astronomy,[1] but they were not long in recognizing that the problem was infinitely more complex for them than for their brothers the astronomers. In astronomy the bodies present are generally few in

[1] In this connection the attempts at chemical mechanics made by Bertholet at the beginning of the nineteenth century may be recalled.

number and the distances between them are great compared with their dimensions. In spite of this great simplicity and in spite of brilliant researches you know that the mathematicians and the astronomers have not yet arrived at a general solution of the problem of three bodies, subjected to the Newtonian attraction; the movements of our planetary system are therefore only determined by approximations. What is to be done then by physicists who find themselves confronted with $3 \times 10^{19}$ molecules when they consider a single cubic centimetre of gas at 0° and at atmospheric pressure? Is it going to be necessary in order to solve this problem to have $3 \times 10^{19}$ simultaneous differential equations each containing about $3 \times 10^{19}$ terms representing, for example, the reciprocal actions of all these molecules two by two? The very thought of such a problem would be sufficient to make the most resolute mathematician recoil with fright. As has been remarked, in a similar connection, by M. Borel in his book *Le Hasard,* if it were desired to examine each of these molecules for only a single second, it would be necessary to devote twenty thousand million human lives to this examination. This example is sufficient to show the practical impossibility of solving such problems in an absolutely general manner.

But if physicists have not been able to follow astronomers to the very end, it should not be imagined that their example has been useless; very much to the contrary, physicists have borrowed from

astronomy and the law of Newton the physics of central forces.

It is thanks to these grandiose conceptions that it has been possible to develop fully certain chapters of physics, such as capillarity, electrostatics, magnetism, etc. Finally, those very fertile conceptions of potential energy and actual energy have been borrowed from celestial mechanics. As it has been so well expressed by Henri Poincaré, "Astronomy has given us a soul capable of understanding nature," and it has been rightly said that Physics is a daughter of Astronomy.

But when the almost insurmountable difficulties of molecular astronomy put obstacles in the way of the enthusiastic flight of physicists the latter had to resign themselves to limiting their ambition somewhat; it was then that the physics of principles appeared.

In this new method of investigation the hope of penetrating into the intimate mechanism of the phenomena is renounced, provisionally at least, and certain principles, which are declared to be absolutely general and which no well-conducted experiment has ever shown to be wrong, are taken as guides. At the present time these principles are already fairly numerous. In particular we have the principle of the conservation of matter (Lavoisier), which teaches us that in all chemical reactions the sum of the weight of the components is equal to the weight of the compound [1]; the principle of the

[1] The principle of the conservation of matter thus enunciated is perhaps that of which the experimental

conservation of energy; the principle of relativity; the principle of the equivalence of work and heat; and so on.

These principles are distinguished from experimental laws in that they are considered to possess an absolute generality; there may be exceptions to an experimental law, but a principle ceases to be a principle if it can be shown that there is a single exception to it.[1] These principles therefore form a powerful means of control in theoretical and experimental researches and a very sure guide which is continually rendering the most eminent services. It is scarcely necessary to say that these principles are not dogmas which have been thrust upon us;

verification is the best established. It has been submitted to the test of the balance and verified with an accuracy of about one in ten million; the experiments carried out for this purpose lasted nearly ten years (Landolt, Manley). It should be observed, however, that on the hypothesis that the mass of a body is proportional to its total energy (see Langevin, *loc. cit.*) this statement must be modified. On this hypothesis the principle of the conservation of mass is more general and merges into the principle of the conservation of energy. It then embraces the case when the mass is a function of the velocity, as for the $\beta$ rays of radium or high-velocity cathode rays.

[1] According to modern ideas the Carnot-Clausius principle (the second principle of thermodynamics) is subject to certain restrictions which are of a more theoretical than practical importance, and which will be discussed in the second part of this essay. That is why it has sometimes been questioned whether it should be classed as a principle.

they are essentially based on experiment and can be overthrown by experiment.

But as the importance of the kinetic theories, the development of which followed the very idea of the granular structure of matter, increased, it was necessary to look for new methods of pursuing investigations further. Faced with the impossibility of applying the laws of rational mechanics to very complex phenomena, physicists have made use of the calculus of probabilities. It must be recognized that the support which this valuable auxiliary has given them has been of such a kind as to repay the trust which they put in it.

## 3. The uncertainties inherent in the calculus of probabilities

The calculus of probabilities has therefore the inestimable advantage that it allows us to pursue our investigations into a domain where the methods of rational mechanics are powerless.

But this advantage is compensated by serious disadvantages. In no branch of mathematics is it easier to make a false step. There are numerous celebrated examples; even when the problems are apparently as simple as those involved in the game of heads and tails. In fact, nothing is easier than to fall into a paradox.[1] There is, however, some

[1] At the foundations of the various games of chance, which may enrich their devotees but which impoverish them with a certainty none the less great, are found precisely these paradoxes, these possibilities. For example:

compensation in these false steps. Sometimes a correct result is obtained from an erroneous hypothesis, that is to say, a result confirmed by experience. It must be admitted in this connection that there are few branches in which mathematics is so generous.[1]

Moreover, the uncertainties which the calculus of probabilities introduces cannot be better demonstrated than by recalling the very definition of probability.

*The probability of an event is the ratio of the number of cases favourable to the event to the total number*

A series of five successive reds has just turned up at roulette. Certain players imagine that it is therefore desirable to stake on black, because, they say, this cannot continue indefinitely and that a series of six reds is extremely rare. It is scarcely necessary to say that this is a great mistake. Experiments show, in fact, that there are on the average as many series of five reds followed by one or more reds as there are series of five reds followed by a black. The probability is thus always one-half. Moreover, Bertrand's saying, "Chance has neither conscience nor memory," should never be forgotten.

[1] Following this train of thought, the first proof which Maxwell gave of the law of the distribution of molecular velocities in a gas may be mentioned. Similarly, in the simplified proof which is given of Boyle-Mariotte's law in the kinetic theory of gases it is assumed that all the molecules have the same velocity, that all collisions are central, and that the molecules can only move parallel to the three edges of a cube, and so on. The correct expression for Boyle-Mariotte's law can be obtained by the use of these three erroneous hypotheses.

*of possible cases, all the possible cases being considered to be equally probable.*

It is this last reservation, necessary though it is, which spoils everything. How can we decide *a priori* that all the possible cases are equally probable ? For the greater part of the time we ignore the intimate nature of the phenomena which we are investigating.

It is true that we may rely on certain considerations of symmetry, on certain intuitions, but in a general way we most frequently issue a *décret d'autorité.* If experiment proves to us *a posteriori* that the results are in accordance with the consequences of our decree we conclude that events indeed occur as if all the possible cases were equally probable.

Let us consider, for example, the various positions which one of the molecules of a gas can occupy in a receptacle under the influence of molecular agitation. We authoritatively declare that the molecule can occupy any position whatever under the influence of molecular agitation and that the probability that it occupies a certain position is always the same.

But what do we actually know about this ? We are absolutely ignorant of the laws which govern the relative displacement of the molecules in the interior of the vessel. Do we know, for example, that a molecule which happens to be in the neighbourhood of the walls of the vessel is not in a different condition ? Are we certain that some molecules do not indefinitely describe periodic

cycles? We cannot know it, but the important thing for us is that the consequences of our decree are all in accord with the results of experiment. If such be the case, we conclude *a posteriori* that we have been right in putting such a hypothesis at the base of our calculus of probabilities.

"These molecules near the walls, or these molecules which describe periodic cycles," we say then, "are probably so few in number that they cannot alter the general consequences which follow from the assumption that we have made."

*Finally, the agreement of the consequences of the hypothesis with experience is the sole criterion which we can invoke in its favour.*

# FIRST PART

## THE PRINCIPLE OF EVOLUTION OF PHYSICO-CHEMICAL PHENOMENA

### 4. Reversible and irreversible phenomena

*Phenomena ideally reversible*

For a phenomenon to be ideally reversible it is necessary in the first place that all the phases of this phenomenon should be capable of successive reproduction and in the inverse direction.

Let us imagine, for example, that we have cinematographed the various phases of a phenomenon and that we make the photographic film travel in the reverse direction, i.e. commencing by the last

exposures obtained. We shall have then an exact representation of what a phenomenon must be to be ideally reversible.

The phenomena of rational mechanics (on condition that we neglect all the thermal phenomena which accompany them, friction, and so on) can give us a very clear picture of ideally reversible phenomena.

We know, in fact, that a pendulum, *if all friction be neglected*, and we only take into account the weight of the bob, must oscillate indefinitely. In this case the oscillation from right to left and that from left to right constitute exactly two ideally reversible phenomena such as we have defined by the cinematograph film.

Similarly, we suppose that, *if we only consider the forces of gravitation*, the motions of the planets around the sun should be reversible. It is sufficient to imagine that, on account of some cataclysm, all the velocities changed sign. The system would then retrace, with equal velocities of opposite sign, all the phases which had preceded the cataclysm.

It is equally apparent that the actions which take place between "ideally" elastic bodies can also afford an image of ideally reversible phenomena.

But on looking closer into the matter, it is ascertained that this ideal reversibility is a limit which is never attained and that something irreversible is invariably connected, in practice, even with phenomena which are apparently the most reversible. In the case of the pendulum we have in reality to take into account the inevitable friction acting at every

instant, which, for example, prevents two successive oscillations having the same amplitude, and from which it follows that for a given position the velocities are no longer exactly equal and of opposite sign.

In the case of the planets gravitating round the sun, even if the supposition of a friction with the ether is ruled out of consideration as too gratuitous, there are still the actions which these bodies reciprocally exert on the fluid masses which enter into their constitution. It is known that these actions can produce a real tendency towards immobility, very slight it is true, and thus they introduce an inherent irreversibility in the phenomena. It is known, in fact, that the work of the tides is produced at the expense of the rotation of the earth. Similarly, in its translatory elliptical motion, every time a planet approaches or recedes from the sun the equilibrium of the fluid masses must be slightly modified, and these periodical deformations must absorb energy and liberate heat just as do the tides; thus they can only be produced at the expense of translatory motion.

Finally, according to the new conceptions to which we have referred (note 1, page 36), as our solar system radiates more energy than it receives its inertia must continually diminish if it be supposed that this diminution is not compensated by a reception of material from other worlds, etc.

But all these thermal phenomena would continue to be produced, and *always in the same sense,* that is in the sense of a liberation of heat, even after

the cataclysm had reversed the velocities. Therefore the progress of the planetary system in the reverse direction would not be ideally reversible.

Thus on closer examination it is seen that the phenomena of rational mechanics completed by thermodynamics do not evade the rule that there are in reality no ideally reversible phenomena.

The same conclusion is reached in the domain of physico-chemical actions.

If a water bath initially at 0° C. and containing a crystal of ice be cooled, the crystal will grow; conversely, if the liquid be reheated the crystal will dissolve and will resume its initial form and dimensions. This is a quite characteristic example of a reversible phenomenon.

But in practice there will never be an ideally reversible phenomenon such as we have defined, for let us recall the conditions of ideal reversibility as stated in classical thermodynamics.

*In order that a system may be ideally reversible it is necessary that every one of the successive states through which it passes should be only infinitesimally different from a state of equilibrium.* Under these conditions only can an infinitely small variation, in one direction or the other, in any phase of the system whatsoever, change the direction of the phenomenon.

In the case of our crystal of ice an infinitely small variation $\pm\, dt$ of the temperature can only change the phenomenon, in the sense of the growth or the disappearance of the crystal, if the crystal and the bath are in equilibrium at 0°. But in

order that this condition should be fulfilled at every instant, it would be necessary, for example, to reheat the bath at an infinitely slow rate. If the supply of heat were not very slow a *finite difference* of temperature $\Delta t$ would be produced between the bath and the crystal, and under these conditions the infinitely small variation $\pm\, dt$ would only produce evolution in the sense of the decrease of the crystal.

In short, in order that an evolution may be an uninterrupted series of equilibrium states it is necessary that the transformation should be infinitely slow. In particular, it is necessary that the temperatures of all the bodies present should only differ from one another to an infinitely small extent at any instant. In other words, it is necessary that thermal equilibrium should be infinitely near to being attained at every instant without being quite attained, because then all transformation would cease.[1]

[1] What we have just said concerning thermal equilibrium applies also to the equilibria involving variables other than temperature. It can be shown, for example, in an analogous manner, that in order to compress a gas by means of a piston in an ideally reversible manner, the difference of pressure between the two faces of the piston $\Delta p$ must be infinitely small at every instant during the compression. But this can only occur if the piston is frictionless, and if this condition were realizable it would still be necessary that it should not possess inertia, because if it could acquire a finite energy the infinitely small variation $\pm\, dp$ would not suffice to change the direction of the motion. We thus get back to the necessity of an infinitely slow evolution.

Therefore such conditions are not practically attainable, so there is ground for stating that, *experimentally, in all phenomena which are the most reversible in appearance, there is some more or less important irreversible part.*

### *Irreversible phenomena*

We have just seen that all phenomena which appear to us to be ideally reversible are, in reality, only imperfectly reversible. But there is a class of phenomena which appear to have lost all reversibility and which are called more especially "irreversible phenomena." We will mention two examples ;

(1) Let us consider first the case of a body falling under the action of its own weight, and stopped in its flight by an obstacle. Experiment teaches us that the energy which it has acquired is generally transformed into vibrations, then into heat, which is slowly dissipated into the surrounding medium.

Let us try to reverse the conditions of the experiment and give the body a quantity of heat energy exactly equal to that which was developed by the stoppage of its flight ; we know that the body would not begin to vibrate and would not ascend to its initial level.

This is a first example of a phenomenon which is very frankly irreversible.

(2) Let us consider two different gases, at the same temperature and the same pressure, and each enclosed in a vessel. Put the two vessels into communication and wait.

At the end of a sufficiently long time we know that the two gases are intimately mixed and our most accurate analyses do not permit us to detect the least difference in the composition of the mixture, no matter from what part of the receptacle we take a sample. Further, if the mixed gases are perfect gases, without chemical action on each other, the mixing will not have given rise to either liberation or absorption of heat; the energy of the mixture of the two gases will be exactly the same as that which the gases would have had separately.

Let us try to reverse the conditions of the experiment and fill our two vessels with a mixture, as intimate as possible, of the two gases, this mixture having the same pressure and the same temperature as before; again establish communication and wait.

We can wait as long as we please but we know that nothing will happen; the mixture remains what it was, a mixture as intimate as before.

Thus we have in the mixture of two gases by diffusion an example of a phenomenon which appears at first sight to be ideally irreversible.

*The irreversibility of biological phenomena.* Although we are not able to follow what happens in a living organism with the same clearness and precision with which we observe the growth or the decrease in size of a crystal, or even the phenomenon of diffusion of two gases into one another, the general conception of irreversibility can be extended into the domain of biological phenomena.

The evolution of a living being, in particular,

presents itself, "on the whole," as an irreversible phenomenon. We always see this evolution taking place in the same sense, from birth to death. We never see this evolution reversed like the cinematograph film just mentioned. We never see the dead revived, an adult progressively becoming an infant, whilst we can voluntarily make a crystal grow or decrease in size in a solution, or transform a liquid into vapour and reliquify this vapour, and so on.

Among all the varied spectacles which nature offers us, why do we never behold the spectacle of the reversibility of life?

For the time being we shall confine ourselves to replying to such a question in the manner of the bachelor of *Le Malade imaginaire* when questioned about the virtues of opium, and content ourselves with saying "it is thus because the evolution of a living being is on the whole an irreversible phenomenon."

But when we say that a phenomenon is irreversible we do not at all mean to assert that its reversibility is impossible. What we do wish to assert is that *its reversibility has never been established and that all the methods hitherto tried to accomplish it have miserably miscarried.*

This attitude, which is entirely in agreement with experience, is moreover irreproachable from the scientific point of view. It was absolutely necessary to state it exactly in order that what follows might be understood.

## 5. The explanation of irreversibility by probabilities

Every one knows that if a white powder and a black powder, initially superposed, are shaken up, a very nearly uniform mixture is obtained at the end of a longer or shorter period. This mixture produces on our eyes the same impression as a grey powder, provided that the observer is at a distance which does not permit him to distinguish between the individual grains. *Since we observe phenomena on this scale* we can say that the agitation of the two powders originally separated has produced a new phenomenon which we call a grey powder.

Once this result has been obtained, experience teaches us that we can prolong the agitation as long as we like but we shall always have a grey powder which does not alter in appearance. On our scale of observation the phenomenon is not further modified, although the grains constituting the mixture occupy different positions every time.

In short, we assert that, experimentally, two powders, black and white, initially separated, can be transformed into a grey powder by shaking, but that this shaking appears to be powerless to produce the reverse transformation, namely, the separation of the grey powder into its original constituents.

In this case, therefore, evolution only takes place in one direction and the mixture of the two powders constitutes, on our scale of observation, an irre-

versible phenomenon, the mechanism of which we shall try to penetrate.

For this purpose let us consider a powder composed only of ten white grains and ten black grains; the grains only differing from one another by their superficial coloration. At the beginning of the experiment these grains are placed in a glass tube (Fig. A); the ten white grains occupying the

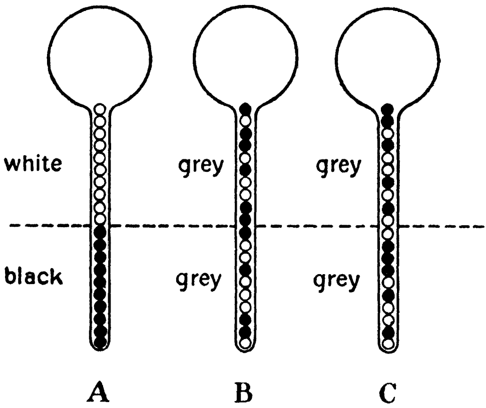


FIG. 1.

upper part of the tube and the ten black grains the lower part. We say that in this initial state the tube is white in the upper part and black in the lower part; this is the phenomenon on our scale of observation.

Let us reverse the apparatus, and after having agitated it sufficiently, replace it in its original position; the white and black grains will be arranged

differently (Fig. B). "At a suitable distance" our tube appears to be grey throughout its length. Let us shake the apparatus up again and return it; we shall again obtain a new arrangement of the black and white grains (Fig. C), but on the scale that we observe the phenomenon, that is to say at a distance, our tube remains grey. Thus the phenomenon is unchanged,[1] and observation shows us that it persists however long we continue this kind of experiment.

The calculus of probabilities will permit us to give an exact interpretation of these facts.

Let us consider the total number of permutations which can be made with only twenty grains; we find that it is

$$P_{20} = 20\,! = 2{,}432{,}902{,}008{,}176{,}640{,}000$$

or approximately:

$$P_{20} = 243{,}290 \times 10^{13}$$

We can therefore arrange the twenty grains of our tube in more than two million million million different ways.

But as we are not in a position to discern the individual grains at a distance, *among all the permu-*

[1] Actually, when the number of grains is very small, as in our example, the nature of the grey powder may be slightly modified. For example, it would be slightly blacker in the upper part in Fig. B than in Fig. C; but these differences become inappreciable to the eye as soon as the number of grains becomes sufficiently great. We shall return to this point later when discussing fluctuations.

*tations that we can imagine there are a considerable number which produce the same impression on our eyes, and which on our scale of observation we call the same phenomenon.*

This can be recognized easily from Table I, in which all the possible permutations are set out.

TABLE I

| Number of white and black grains in one of the halves of the tube, the upper half, for example.[1] | | | | Corresponding number of permutations. | Probability of the appearance of one class of permutations. |
|---|---|---|---|---|---|
| 10 | white | 0 | black | $1 \times A$ | 0·0000 054 |
| 9 | ,, | 1 | ,, | $100 \times A$ | 0·0005 4.. |
| 8 | ,, | 2 | ,, | $2025 \times A$ | 0·0109 7.. |
| 7 | ,, | 3 | ,, | $14400 \times A$ | 0·0780 ... |
| 6 | ,, | 4 | ,, | $44100 \times A$ | 0·2388 ... |
| 5 | ,, | 5 | ,, | $63504 \times A$ | 0·3439 ... |
| 4 | ,, | 6 | ,, | $44100 \times A$ | 0·2388 ... |
| 3 | ,, | 7 | ,, | $14400 \times A$ | 0·0780 ... |
| 2 | ,, | 8 | ,, | $2025 \times A$ | 0·0109 7.. |
| 1 | ,, | 9 | ,, | $100 \times A$ | 0·0005 4.. |
| 0 | ,, | 10 | ,, | $1 \times A$ | 0·0000 054 |
| | | | | $184756 \times A$ | 1·0000 ... |

$$A = 10!\,10! = 13,168,189,440,000 = 1{\cdot}3 \times 10^{13}$$

[1] The number of permutations corresponding to each class is given by the formula $N = C^n_{10} \cdot C^{10-n}_{10} \cdot A = (C^n_{10})^2 \cdot A$; $C^n_{10}$ is the number of combinations of 10 grains taken $n$ at a time; $n$ thus varies from 1 to 10 according to the class of the permutations. In this example we have supposed that the white and black grains only differ from one another in superficial coloration, so that it can be assumed that all the possible combinations are equally probable. This would no longer be the case if the black grains had a greater density than the white ones; in such an event

This table shows us, in the first place, that among all the possible permutations there are A, i.e. about $10^{13}$, which lead to the ten white grains being in the upper half and consequently the ten black grains being in the lower half of the tube.

This is the number of permutations which are capable of leading back to the initial state, that is to say to the original separation of the black and white powders (Fig. A).

Although the number A is very great in absolute value it is nevertheless incomparably small with respect to the total number of permutations $P_{20}$. It is even very small with respect to the number of permutations which lead to five white and five black grains being in each half.

It is obvious that this last class of permutations is that which gives the lower half of the tube the same colour as the upper half; it is this which is the most numerous class of permutations and which is consequently the most probable.

Thus, as our table indicates, it would be necessary to shake up the tube 184,756 times "on the average" in order to have one chance of getting back to an *initial equivalent state*, that is, a state producing the same impression on our eyes. If we only agitate the tube once the probability that this agitation will produce this initial state will thus be 1 : 184,756, and

all the permutations would not be equally probable and the law of distribution would not be that given by Table I. The mixture of the greatest probability would be then probably a little darker in the lower half than in the upper half.

we say that *the probability that the phenomenon is reversible on our scale of observation is* 1 : 184,756.[1]

Table I shows us further that the permutations which lead to five black and five white grains in the lower or upper part of the tube, and which are the most numerous, are 63,504 times more frequent than those which correspond to the complete separation of the two kinds of grains (initial state).

It will now be understood why the phenomenon only evolves in one direction and *why it is irreversible.*

If the separation of a grey powder into its two constituents does not occur when it is agitated *it is not because the phenomenon is impossible but because it is only very slightly probable.*

When the grains which constitute the grey powder are fairly numerous the probability of a return to the original separation becomes so small that we do not hesitate to say that the phenomenon is impossible, though in reality it is only extremely slightly probable.

Such are the conclusions at which we arrive when we consider powders composed of even relatively small numbers of grains.

[1] We can go further. Let us suppose that we have numbered the grains; in order to get back to an *identical initial state*, i.e. such that the same grains occupy the same positions as in the initial state, it would be necessary to agitate the tube at least $P_{20}$ times. In other words, the probability of the return to this identical state would be $1 : P_{20}$ or $1 : 243{,}290 \times 10^{13}$. But such a return only concerns us slightly if we cannot distinguish the individual grains at a distance.

But the preceding considerations interest us from another point of view. They show us in a tangible manner that a phenomenon (white, black, or grey powder) can only be considered as *the appearance which the laws of chance assume, on our scale of observation.*

But what is to be understood by "laws of chance"? As Poincaré has very well expressed it, the expression "laws of chance" means, not necessarily the absence of laws, but laws of which the effects are so complex that their detailed analysis completely escapes us and that we can only grasp with difficulty the general resultant tendencies of a very large number of partial effects which, to some extent, counterbalance each other.[1] In particular, such are the almost infinitely complex effects of the agitation of powders, which are capable of arranging only twenty grains in a tube in more than two million million million different ways.

In addition, the laws of chance are not incompatible with a rigorous determinism; we shall return to this point later (§ 16).

In short, the example of the powders shows that it is essentially *the scale of observation which creates the phenomenon* (appearance).

Closely connected, therefore, with the mystery of these laws of infinitely complex effects is the no smaller mystery of the thinking being, without which neither scale of observation nor, consequently, the phenomenon could exist.

The foregoing shows how the calculus of prob-

[1] On the laws of chance, see Poincaré, Science et Méthode.

abilities easily leads us to coast along the shores of metaphysics ; moreover, this will not be the last time that it will carry us towards these rocky shores.

### 6. The irreversibility of physico-chemical phenomena

If the argument which we have applied to a small number of grains be extended to molecules, incomparably more numerous and subject to mutual forces the complexity of which escapes us, it will easily be understood why certain physico-chemical phenomena are frankly irreversible ; in other words, why the inverse phenomenon is never observed.

*First example.* Let us reconsider the case of the diffusion of two gases into one another. Let us assume *a priori* (although, as has been said, we are completely ignorant of the nature of the forces which govern the relative displacements of the molecules of the gas)—let us assume that all the permutations of position which are possible with the molecules of these gases are equally probable.

Among these innumerable permutations,[1] those which produce a mixture so uniform that any analysis, made on any part whatsoever, cannot detect any heterogeneity, are prodigiously numerous relative to those which correspond to a heterogeneity which can be detected by experiment. This is the problem

[1] As one cubic centimetre of gas at 0° and 760 mm. contains $3 \times 10^{19}$ molecules, the number of permutations which can be made with the same number of grains would be $3 \times 10^{19}\,!$ ; this number cannot be appreciated.

of the mixture of two powders, but with a number of elements incomparably greater. It can be asserted, therefore, with an infinitely small risk of being wrong, that the diffusion will evolve in the direction of a mixture as "uniform" as can be defined by the exactness of analysis.

The risk will be smaller still if we say that two gases, once mixed, do not separate of themselves; the probability of this spontaneous separation is then so small that our assertion is equivalent to an almost absolute certainty, and there is no fact of which we are more certain.

*Second example.* A body falls in a vacuum under the action of its own weight; it is stopped in its flight by an obstacle and the kinetic energy which it has acquired is transformed into heat. Let us leave it to cool and then communicate to it a quantity of heat energy equal to that developed by the stoppage. Experiment, repeated as often as we like, shows that the body does not move under the action of the heat energy which is communicated to it. We say that the phenomenon is irreversible.

But, as in the preceding case, the reason of this irreversibility can be found in a problem of probabilities, though the phenomenon is terribly complex.

In the first place, let us try to set out the facts which are involved. Firstly, when the body was falling under the action of its weight, its molecules assumed, independent of their motion of thermal agitation, a collective velocity *directed* from above to below; it is to this collective velocity that what is

called in mechanics its *vis viva*, its kinetic energy, is due.

Then, immediately the body struck the obstacle, this directed kinetic energy was transformed, by means of the unknown molecular forces (equivalent in their complexity to a kind of agitation), into an *uncoordinated motion*, that is to say, into a motion distributed approximately equally in all directions ; this motion being added to the thermal agitation, the temperature of the body rose.

On the other hand, it is again uncoordinated motion which is communicated to the body when it is heated, with the chimerical hope of causing it to re-ascend to its original level ; and this motion is incapable, by the very fact of its symmetrical distribution, of giving rise to an appreciable motion of the whole in any direction whatever, much less raising the body to its initial level.

Nevertheless, this last eventuality should not be immediately set aside. Let us try to state the conditions which would permit the body to re-ascend to its initial level.

It might be supposed, for example, that by a singular coincidence, at a given instant, all the molecules which constitute the body and the obstacle might occupy the same positions as at the instant of collision, and that their velocities might be equal and of opposite signs to those which they possessed at that instant ; the molecular forces being assumed to be central forces.

But this distribution would certainly not be the only one capable of causing the body to re-ascend.

An infinite number of others can be imagined, seeing that the fall never, so to speak, takes place twice under absolutely identical conditions from the point of view of the succession of molecular movements. Nevertheless, all these distributions would have one character in common, namely, that of presenting a very great dissymmetry of the components of the velocities directed upwards. Thus we are right in asking the following fundamental question, a question, moreover, which we shall refrain from answering :

*Can such a singular and dissymmetrical distribution of velocities be produced by thermal agitation alone ?*

To this question the opponents of the new conceptions, without knowing anything further of the laws of thermal agitation, will be ready to assert definitely that it is absolutely impossible for thermal agitation to produce such a distribution. It will be impossible to contradict them.

On the other hand, the partisans of the new conceptions, also without knowing anything further about the mechanism of thermal agitation, will declare, equally definitely, that thermal agitation can bring about any distribution of velocities, no matter what, so long as the total energy remains constant. "But," they say, "these dissymmetrical distributions such as those which are capable of projecting the body upwards from below, although considerable in number, are incomparably less numerous than the symmetrical distributions which leave the body apparently motionless ; just as in the example of the powders, the permutations which

lead to the ten grains being in the upper half are incomparably less numerous than those which correspond to a uniform mixture. The proof that our view is probable," they will add, "is that thermal agitation is actually capable of throwing very small particles upwards, as is seen in the Brownian movement. Therefore, in this case, more favourable to the dissymmetric distribution of velocities, the phenomenon can indeed be produced. It is a question of more or less, but the phenomenon is possible." And they will repeat with Herodotus and Amiel: "If one is sufficiently lavish with time, everything possible happens."

Such appears to be, at the present time, the point of view which dominates the thoughts of physicists concerning irreversibility. Moreover, this conception can be extended to all irreversible phenomena, even indeed to the irreversibility of biological phenomena.[1]

## 7. The second principle of thermo-dynamics considered as a principle of evolution

Let us consider, now, how the conception of irreversibility is connected with the second principle of thermodynamics.

The definitions which have been given of the

[1] Leaving the domain of physics and going to extremes, it can be supposed that infinitely complex laws are capable of producing all phenomena, that is to say, all phenomena

second principle are very often incomplete ; in fact, it is difficult to state it in a way which is at once general, rigorous, and sufficiently suggestive ; in addition, this principle has often been defined by one or other of its consequences (see Planck's *Thermodynamics*).

*Examples :* Heat cannot pass by itself from a cold body to a hot body without the production of some correlative modification.

It is impossible to conceive a thermal machine continuously transforming heat into mechanical work without the existence of at least two sources at different temperatures.

The quantity of energy which can be transformed into mechanical work is continuously diminishing; energy degrades itself and the universe tends towards immobility. . . . And so on.

Clausius appears to have been the first satisfactorily to define Carnot's principle, by introducing the conception of entropy. The second principle thus became *the principle of the increase of entropy*, or the Carnot-Clausius principle.

We do not wish to enter here into all the considerations which even the definition of entropy necessitates. We shall confine ourselves to recalling some ideas absolutely indispensable to our purpose.

Let us consider an *isolated system*, which we can

which can be imagined, but with a degree of probability varying within almost infinite limits.

*All will be*, all seems to be, and all is only nothingness.

This is a thought of Buddha ; we are now quite in the domain of metaphysics.

choose as large as we please ; our visible universe, for example.[1] For every state through which this system passes there exists *a function the value of which depends only on the actual state of the system*, and to which Clausius has given the name of *entropy ;* we shall designate it by $S$.

We only know the value of this entropy with respect to a constant. In other words, we no more know the absolute value of the entropy of a body than we know the absolute value of its energy or its velocity. The variations of entropy, of energy, of velocity, etc., are what we can determine experimentally.[2]

Further, *when a system is in equilibrium its entropy is a maximum ; this involves the condition* $dS = 0$.

But what is particularly characteristic of the *entropy function* is that it *can only increase when physico-chemical phenomena occur in the interior*

[1] It is necessary to observe, in this connection, that a system of infinite extent tends to approximate to an isolated system. In fact, it may be assumed as a first approximation that the *external forces* which act on it are proportional to its exterior surface, i.e. *to the square of its radius*, if it be supposed to have a spherical form. On the other hand, the forces which are produced in *the interior* of the system are proportional to its volume, i.e., *to the cube of the radius*. When the radius tends to become infinite the external forces become negligible with respect to the internal forces, and the system approaches the conditions of an isolated system (Planck's *Thermodynamics*).

[2] Let it be remembered, however, that Nernst has been led to suppose that the entropy of bodies (liquid or solid) should be zero at absolute zero.

*of the system.* It is this change of entropy always in the same direction which has justified the second principle of thermodynamics being frequently called a *principle of evolution.*

From this point of view it is useful to recall the form in which the second principle of thermodynamics has been stated by Langevin and Perrin. They say that by virtue of this principle *an isolated system cannot pass twice through exactly the same state.* This latter statement brings out particularly clearly the evolutionary character inherent in the second principle.

But the point on which we would insist is the way in which the idea of irreversibility is connected with the second principle.

Clausius has shown that when an isolated system passes from one state to another *the entropy can only increase if irreversible phenomena take place in the interior of the system*, so that the increase of entropy is a kind of measure of the irreversibility.

If all the phenomena which take place in the interior of the system were ideally reversible the entropy would remain constant. But we have seen (4) that this is a limiting case, never realized. In practice, there is something irreversible in all physico-chemical transformations, so that in reality the entropy of the system will not remain constant but will continually increase.

## 8. The physico-chemical phenomena which take place in the interior of an isolated system tend to make this system evolve towards states which are more and more probable

This was approximately the state of the problem, in its main outlines, when the researches of Gibbs and Boltzmann appeared.

Boltzmann's achievement is to have shown that the entropy $S$ of an isolated system was connected with the probability $p$ of its actual state by the relation

$$S = K \log_e p + C,$$

$C$ being an undetermined constant (see note 1, pages 66 and 67).

In other words, the variable part of the entropy of a system is proportional to the logarithm of the probability of the state in which it exists. It follows immediately that the change of entropy between two successive states is proportional to the difference between the logarithms of the probabilities of these two states. Thus

$$S_2 - S_1 = K\ (\log_e p_2 - \log_e p_1) = K \log_e \frac{p_2}{p_1}$$

As $S_2 - S_1$ is always positive, since the entropy of an isolated system can only increase, it follows that $p_2$ is greater than $p_1$; i.e. that the second state is more probable than the first.

To say that in passing from the first state to the second the entropy has increased is thus to assert

that *the system has evolved to a more probable state.*

If the system is now left to continue its evolution under the action of the physico-chemical phenomena which take place in its interior, it will end by attaining a state of equilibrium. At that moment, thermodynamics tells us that *the entropy is a maximum ; it will therefore be the same with the probability, which corresponds to the state of equilibrium.*

In fact, this is what has been established in the case of the mixture of the white and black grains ; the equilibrium attained by the agitation corresponds, indeed, to the most probable class of permutations, those which result in a uniform mixture in the two halves of the tube. This uniform mixture may be said to constitute the equilibrium position of the system under the action of the agitation.[1]

In short, classical thermodynamics teaches us that *in an isolated system the entropy can only increase and that this increase in the entropy is always correlative of irreversible phenomena which occur in the interior of the system.*

On the other hand, we have seen (5) that *the*

[1] It is very evident that the system of powders which are agitated does not constitute an isolated system, the action which produces this agitation being exterior to the system. We have had recourse to this comparison, nevertheless, because it allows us to follow the detail of the modifications which are produced. The system of two gases diffusing into one another affords a more rigorous comparison, and one which leads to the same conclusions. In this case, it is the molecular agitation in the interior of the system which produces the mixing and the system can very well be considered as an isolated system.

*passage from one state to another by an irreversible path corresponds to the passage from a less probable state to a more probable state.* By combining these two propositions we can see that the increase of entropy must correspond to the passage from a less probable to a more probable state. Boltzmann clearly demonstrated this by showing that *the increase in the entropy is proportional to the difference between the logarithms of the probabilities of the two successive states considered.*

Finally, it results that by virtue of the second principle *the physico-chemical phenomena which occur in the interior of an isolated system have the effect of making the system evolve towards states which are more and more probable.* But, as will be seen in the second part of this paper, this consequence is not absolute and it is modified by the phenomenon of fluctuations.

*Note* 1.—We think it well to reproduce here the outlines of the reasoning which leads to the fundamental formula

$$S = K \log_e p + C.$$

If an isolated system composed of a large number of corpuscles (molecules, atoms, etc.) and containing a fixed quantity of energy be considered, the equilibrium state of the system is distinguished from all others by the fact that its probability is a maximum (Boltzmann). Moreover, we have established this for the mixture of a powder containing an equal number of white and black grains; the equilibrium corresponds to the uniform grey mixture of greatest probability.

On the other hand, it is shown in thermodynamics that

the entropy of a system is a maximum in the equilibrium state.

There is, therefore, a parallelism between the probability of the actual state of the system and its entropy; and this parallelism must be maintained whatever the system and whatever the conditions of equilibrium. The conclusion is drawn that *the entropy of a system is a universal function of its probability* (Drude, *Optique*, II, p. 274).

It remains to determine the form of this function. It can be obtained easily by the following reasoning (Planck, *Vorlesungen über Theorie der Warmestrahlung*, 1906, p. 136).

Let $S_1$ and $S_2$ be the entropies of two isolated systems, each absolutely independent of the other; and let $S$ be the entropy of the two systems considered as a single system; then

$$S_1 = f(p_1)\,; \quad S_2 = f(p_2)\,; \quad S = f(p)\,;$$

$p_1$, $p_2$, and $p$ being the respective probabilities of the actual states of the two systems separately and as a whole.

On the other hand, the probability $p$ that the two systems will exist "simultaneously" in the states 1 and 2 is, by a well-known theorem, the product of the two probabilities; and thus $p = p_1p_2$.

As, moreover, the entropy $S$ of the two systems considered as a whole is equal to the sum $S_1 + S_2$ of the entropies of each of them separately, we have

$$f(p_1p_2) = f(p_1) + f(p_2).$$

Differentiating this expression with respect to $p_1$ ($p_2$ remaining constant) and then with respect to $p_2$ ($p_1$ remaining constant), we obtain finally

$$p_1p_2f''(p_1p_2) + f'(p_1p_2) = 0$$

or

$$pf''(p) + f'(p) = 0.$$

The integral of this differential equation is

$$f(p) = K \log_e p + C.$$

This is the expression for the entropy $S$.

# SECOND PART

## THE LIMITATIONS OF THE PRINCIPLE OF EVOLUTION

### 9. Fluctuations in the game of roulette [1] (heads and tails)

In order to bring out more clearly some of the essential characteristics of fluctuations we will study them in the relatively simple case of the game of roulette (heads and tails).

Suppose that a player always places his stake (one shilling, for example) on the red and plays for a series of $2m$ spins. At the end of the series he finds that he has won (or lost) on $N$ spins.

The *difference* $N - m$ between the number of spins on which he has won (or lost) and the number on which he would have required to win in order to retire from the game without gaining or losing, *represents his gain* (*or his loss*) *;* it is the *fluctuation* for the series.

Let us consider now a very large number of persons each playing under the same conditions for a series of $2m$ spins. Some will retire from the game having won, others will have lost, and finally others,

[1] In the discussion which follows we shall suppose that the white, which enriches the bank, is suppressed. From the point of view of probabilities this game of roulette is exactly equivalent to the game of heads and tails.

having won and lost exactly $m$ spins, will retire without having either gained or lost.

Let us now take the sum $\Sigma(N - m)$ of all these differences, whether they concern gains or losses, and let us divide this sum by the total number of players, including those who have neither gained nor lost. The quotient thus obtained will be the *mean fluctuation* $\varepsilon$, that is to say, the gain or loss which a player makes "on the average" in a series of $2m$ spins; $\varepsilon$ is sometimes called his "mathematical expectation."

If we now consider longer and longer series of spins the calculus of probabilities leads to an important conclusion, namely, that the mean fluctuation increases proportionally to the square root of the number $2m$ of spins in the series.

This result and the consequences which it involves are clearly shown in Table II.

TABLE II

| | $m = 100.$ | $m = 10{,}000.$ | $m = 1{,}000{,}000.$ | $m = 100{,}000{,}000.$ |
|---|---|---|---|---|
| $\varepsilon$ | 5·64 | 56·4 | 564 | 5,642 |
| $\sqrt{m}$ | 10 | 100 | 1,000 | 10,000 |
| $\frac{\varepsilon}{m}$ | 0·056 | 0·0056 | 0·00056 | 0·000056 |
| $\frac{m+\varepsilon}{m}$ | $1 \pm 0{\cdot}056$ | $1 \pm 0{\cdot}0056$ | $1 \pm 0{\cdot}00056$ | $1 \pm 0{\cdot}000056$ |

We draw the two following conclusions from these figures:

(1) *The absolute value $\varepsilon$ of the gain or the loss which a player makes "on the average" is greater the greater the number of spins in the series; it increases proportionally to the square root of the number of spins in the series.*

It immediately follows that "on the average" the longer a player continues to play the greater are his chances of enriching or of impoverishing himself; but this enrichment or this impoverishment is not proportional to the time for which he plays, but to its square root. This result appears to be peculiar at first sight, but it is explained by the fact that compensation spins occur in long series which generally do not arise in the shorter series.

(2) In the second place, we see that the ratio $\frac{m \pm \varepsilon}{m}$ (between the number of spins on which a player has won or lost, and the number of winning or losing spins which the chance of the game assigns him) *is nearer to unity the larger the number of spins in the series.* This follows immediately from the fact that $\varepsilon$ is proportional to $\sqrt{m}$; the expression $\frac{m \pm a\sqrt{m}}{m}$ tending towards unity when $m$ becomes very great.

This second expression is essentially only one of the forms of *the law of large numbers* which was stated for the first time by Daniel Bernoulli.

To sum up: though the player's gain or loss increases "on the average" as the game is prolonged, the ratio of the number of spins on which he has

won to the number of spins on which he has lost tends towards unity. In addition, this ratio does not affect the state of the player's bank; only the absolute value of the fluctuation at the end of the series enriches or impoverishes him.

These considerations will permit us to attack the problem of fluctuations in physico-chemical phenomena, but we will first examine what happens in the more concrete example of the mixture of powders.

## 10. Fluctuations in the mixture of two powders

Let us examine more closely, therefore, what happens when an intimate mixture of black and white grains is agitated.

Table I (page 52) shows us that the most probable permutations, and consequently those which appear most frequently, are the ones which result in five black and five white grains being in each half, that is, those which correspond to a uniform mixture of the two kinds of grains. But these are not the only ones; the permutations which yield six white grains and four black grains in the upper half and six black grains and four white ones in the lower half, or vice versa, will also arise, though less often. The permutations of seven white grains and three black ones, etc., will appear more infrequently, and so on. The probabilities of the appearance of each kind of permutation are given in column 3, Table I.

Briefly, during all the time that the tube is agitated, *the composition of the mixture which fills each*

*half of the tube will oscillate round the most probable value*, which, we have seen, corresponds to a uniform mixture, or to what can be called the theoretical equilibrium. These oscillations round the most probable value, that is to say round the position of equilibrium, are now called fluctuations.

Essentially, the effect of these fluctuations will be to make the mixture in one half of the tube sometimes whiter, sometimes blacker than the uniform mixture of greatest probability, in the same way as the game of roulette has the effect of making the player sometimes richer, sometimes poorer than the chance of the game would indicate.

*Mean value of the amplitude of the fluctuations*

In a large number of problems it is useful to know the mean value of the amplitude of the fluctuations.

In the case of our powder of twenty grains it can easily be deduced from the following table:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 63,504 A | fluctuations | of | amplitude | 0 | grains = | — |
| 2 × | 44,100 A | ,, | ,, | ,, | 1 | ,, = | 88,200 A |
| 2 × | 14,400 A | ,, | ,, | ,, | 2 | ,, = | 57,600 A |
| 2 × | 2,025 A | ,, | ,, | ,, | 3 | ,, = | 12,150 A |
| 2 × | 100 A | ,, | ,, | ,, | 4 | ,, = | 800 A |
| 2 × | 1 A | ,, | ,, | ,, | 5 | ,, = | 10 A |
| | | | | | | | 158,760 A |

The mean value of the fluctuation is:

$$\varepsilon = \frac{158{,}760\,A}{184{,}756\,A} = \pm\ 0{\cdot}86 \text{ grains.}^{1}$$

[1] The calculation is carried out by multiplying the probability of each kind of fluctuation (Table I, column 3) by its amplitude and summing all these products.

That is to say, the composition of the mixture during a " very long series of agitations " will differ " on the average " from the uniform mixture by $\pm 0{\cdot}86$ black or white grains.

If, now, we examine how the mean fluctuation $\varepsilon$ varies *when the number of grains which constitutes the powder becomes greater and greater*, i.e. when the powder which fills the tube is finer and finer, we find a result analogous to that mentioned in the case of roulette, that is, that *the absolute value of the mean fluctuation continually increases; it increases proportionally to the square root of the number of grains.*

Thus, if a powder of 20 grains gives a mean fluctuation of $\pm$ 0·86 grains, a powder of 100 grains will give a mean fluctuation of approximately $\pm 0{\cdot}86 \sqrt{\dfrac{100}{20}} = \pm 1{\cdot}92$ grains, and so on.

*The law of large numbers*

Let us now designate the total number of grains in our powder by $2m$ ($m$ being the number of grains of each colour). If we consider the mixture in one of the halves of the tube, the number of grains of each colour which corresponds to the most probable mixture will be $\dfrac{m}{2}$ (5 in the case of the powder of 20 grains).

The ratio $\dfrac{\dfrac{m}{2} \pm \varepsilon}{\dfrac{m}{2}}$ will tend towards unity the

greater the value of $m$, as in the game of roulette; as before, this results from the fact that $\varepsilon$ increases proportionally to the square root of $m$.

In other words, when the number of grains of which the powder is composed is indefinitely increased, the influence of the mean fluctuation on the composition of the mixture becomes smaller and smaller and finally becomes negligible. Therefore, the composition of the powder tends more and more to become that which corresponds to the most probable mixture, to that which has been called the equilibrium.

### *Graphical representation of the distribution of fluctuations*

With the help of Table I (in which are given all the possible permutations) we can draw a curve, taking as ordinates the number of permutations of each category and as abscissæ the deviation of the corresponding composition of the mixture from the most probable value of this composition. For example, the permutations which result in seven white grains and three black grains in the upper part of the tube have a deviation of $+2$ white grains from the most probable value of the mixture, which is five white grains and five black grains; we shall therefore take as abscissa the value 2 and as ordinate 14,400 $A$.

The curve thus obtained is shown in Fig. 2. It is symmetrical on either side of the most probable value, which indicates that the probability of a

positive deviation is in this case equal to the probability of a negative deviation of the same amplitude.

In addition, the most probable value of the mixture is equal to its mean value ; this follows immediately from the symmetry of Table I on either side of the maximum value.

It should not be imagined, however, that all curves showing the distribution of deviations round the most probable value are necessarily symmetrical,

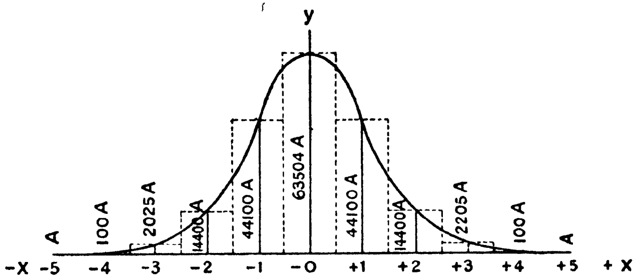


FIG. 2.

as in the case of the mixture of powders, or that of the game of roulette, which we have so far considered.

The curve showing the distribution of the molecular velocities in a gas (for example) round the most probable value (Maxwell's distribution law) is not at all symmetrical ; and it is known that the most probable velocity is not coincident with the mean velocity. The curve in Fig. 2 is therefore only a particular case of the distribution of deviations, but a particularly important case.

The ordinates of this curve are proportional to the squares of the coefficients of the binomial equation (see the formula, footnote, page 52); or

$$1 + (C_m^1)^2 + (C_m^2)^2 + \dots + (C_m^{m-1})^2 + 1 = C_{2m}^m$$

and the curves come within the category of symmetrical probability curves.[1]

Finally, it may not be without value to remark that all the curves showing the distribution of deviations which are symmetrical on either side of the most probable value are not necessarily in this class.

*Analytical representation of the distribution of fluctuations*

When the number of ordinates of the curve becomes very large (that is, when the number $2m$ of grains constituting the powder greatly increases), it is generally advantageous to represent the distribution of the velocities by a continuous function

$$y = f(x).$$

In the case of the powders and that of the game of roulette this expression is of the form

$$y = Ce^{-k^2x^2} \qquad (1)$$

where $C$ and $k$ are two constants.

[1] In the game of roulette the ordinates of the curve showing the distribution of the deviations round the most probable value are directly proportional to the coefficients of the binomial equation

$$1 + C_m^1 + C_m^2 + \dots + C_m^{m-1} + 1 = (1 + 1)^m$$

The curve obtained is also a symmetrical probability curve.

It is important to observe that the formula (1) is only applicable if the grains are sufficiently numerous. In addition (and it is well to remember this) *the formula is entirely deduced from the laws of combinations, permutations, and the like; it rests on no other hypothesis.*[1]

Usually, in the theory of probabilities, the expression (1) is put in a more convenient form by writing it $C = \frac{Nk}{\sqrt{\pi}}$; $N$ being a new constant, the significance of which in the problem of the powders will be shown presently. The formula (1) then becomes

$$y = \frac{Nk}{\sqrt{\pi}} e^{-k^2x^2} \tag{2}$$

In the case of the problem of the powders $k = \frac{2}{\sqrt{m}}$.[2]

It is easy to see that the constant $N$ represents the total number of permutations which can be made with $2m$ grains.

In fact, the area contained between our curve and the axis of $x$ represents the total possible number of permutations.

Thus, by definition we have

$$P_{2m} = 2 \int_0^\infty y \, dx.$$

[1] Borel, Éléments de la théorie des probabilités, p. 48.

[2] In the case of the game of roulette we have $k = \frac{1}{\sqrt{m}}$.

Substituting in this expression the value of $y$ given by (2) and integrating,[1] we obtain

$$P_{2m} = N.$$

The mean fluctuation can also be explained by means of the continuous function (2). In fact, this mean fluctuation is by definition equal to the sum of all the deviations (taken without respect to their signs) divided by the total possible number of permutations. It can thus be expressed by

$$\varepsilon = \frac{2\int_0^\infty x\ y\ dx}{2\int_0^\infty y\ dx} = \frac{\int_0^\infty x\ e^{-k^2x^2}dx}{\int_0^\infty e^{-k^2x^2}dx}$$

By integrating we have, finally,

$$\varepsilon = \frac{1}{k\sqrt{\pi}} = \frac{1}{2}\sqrt{\frac{m}{\pi}} \pm a\sqrt{m}$$

It follows immediately that the ratio

$$\frac{\frac{m}{2} \pm \varepsilon}{\frac{m}{2}}$$

[1] It is known that the definite integral $\int_0^\infty e^{-k^2x^2}dx$ has the value $\frac{\sqrt{\pi}}{2k}$.

tends towards unity as $m$ increases, as is required by the law of large numbers.

## 11. Fluctuations in physico-chemical phenomena

We shall confine ourselves to giving some examples.

(*a*) *The displacement of the particles in the Brownian movement.* It is known that the disordered agitational motion which is observed when very small particles are suspended in a fluid is attributed to the collisions of these particles with the molecules of the fluid, caused by thermal agitation. But the essential characteristic of this movement is its absolute irregularity.

In fact, the trajectory of a single particle cannot be predicted by any means whatever. At each collision a sort of roulette problem is presented. Will this collision have the effect of making the particle ascend or will it make it descend ? will it send it to the right or to the left ? will the resulting displacement be greater or less than the mean displacement which in general results from a collision ? and so on. We can no more reply to all these questions than we can say in a spin at roulette the red will turn up rather than the black.

But let us observe the position of the particle at the end of a time $t$. If all the actions were rigorously compensated the particle would be found in its initial position ; but this case is relatively very rare when the number of collisions is considerable ; in the same way as it is very rare for a player

to retire from the game of roulette after a considerable number of spins without gain or loss. What causes the displacement of the particle, just as it impoverishes or enriches the player, is the absolute value of the fluctuation ; in the case of the Brownian movement it is the collisions which do not compensate each other's effects.

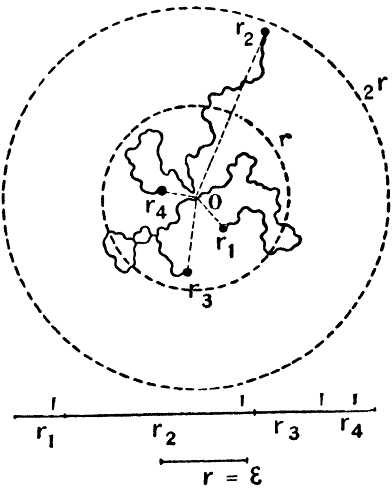


FIG. 3.

For example, let 1, 2, 3, 4, . . . (Fig. 3) be the trajectories of a large number of identical particles which start successively from the same origin O. Let us suppose that we are able to photograph these trajectories during all the time $t$ for which we observe each of them.

We should then see that at the end of this time $t$ some are relatively far from the origin and that others have nearly or quite returned thereto. But "on the average" they will be at a distance $r$ away from it, given by the expression

$$r = \frac{r_1 + r_2 + r_3 + \ldots}{N} = \varepsilon,$$

$N$ being the total number, supposed very great, of the particles; $\varepsilon = r$ is then the *mean fluctuation.*[1]

In order that this mean fluctuation should have twice the value, $2r$, it is necessary that there should be four times the number of collisions under the same conditions, that is, that we should observe for a time $4t$. Similarly, in the game of roulette it is necessary to quadruple the number of spins in order to double the absolute value of the mean fluctuation.

We thus obtain the law of the Brownian movement proved by Einstein

$$\frac{r^2}{r'^2} = \frac{t}{t'},$$

a law which under different forms is verified by experiment, and of which the laws of diffusion can be considered as an immediate consequence.

(*b*) *Critical opalescence.* In the neighbourhood of the critical point there is very often observed an

[1] In Fig. 3 the number of particles has been reduced to four for the sake of clearness; but it is obvious that the law of the Brownian movement could not be deduced from the observation of such a small number of particles.

opalescence phenomenon which is very largely analogous to the well-known Tyndall's phenomenon. This is, that at the moment of liquefaction the fluid medium becomes opalescent; it scatters light in the same way as a clouded solution containing particles in suspension; and, as is well known and can be shown experimentally, this more or less bluish light is polarized.

This critical opalescence phenomenon is actually attributed to *fluctuations of density*. In fact, at the critical point the coefficient of compressibility tends to become infinite; it follows that the least accidental change in the pressure produces a very appreciable variation in the density at any point in the fluid. Therefore instead of the medium behaving as if it were homogeneous it will behave as if it were composed of a very large number of elements of different density, greater or less than that which corresponds to equilibrium; and these elements of different density will have the same effect on the incident light as the particles in suspension in a clouded solution; whence the phenomenon of opalescence.

(*c*) *The blue of the sky.* According to Einstein's theory the blue colour of the sky and the polarization of its light is also to be attributed to fluctuations of density, that is to say, to a phenomenon of the same nature.

Now in these two cases the calculation of the fluctuations, based on probabilities, leads to consequences which are in good numerical agreement with the results of experiment.

It would indeed appear that in the Brownian movement there is an experimental proof of the actual existence of fluctuations.

*Important note.* The investigation into the game of roulette which is summarized in Table II (p. 69) indicates that the ratio $\frac{m \pm \varepsilon}{m}$ differs more from unity the smaller the number of spins in a series. The smaller this number the more "relatively" important are the fluctuations. The consideration of the mixture of the two powders has led us to the same conclusion.

Similarly, in the fluctuations of density, the ratio of the density of an element of volume to the mean density of the fluid will differ more from unity the smaller this element and the fewer the molecules concerned.

As the number of molecules concerned in physico-chemical phenomena is always considerable, it follows that, in general, it would be necessary to be able to choose an extremely small element for the relative importance of the fluctuations to be appreciable.

*Thus in the majority of cases fluctuations cannot be observed experimentally on account of the smallness of the space and of the time which can be devoted to the experiment.*

### *The generality of the phenomenon of fluctuations in physical chemistry*

Though the phenomenon of fluctuations has only been detected experimentally in a small number of cases in physical chemistry, it is nevertheless permissible to consider it as a general phenomenon, inherent in all the kinetic theories which involve the conception of mobile equilibrium, that is to say, in all the kinetic theories of physical chemistry.

In this paper we have limited ourselves to the consideration of fluctuations of coloration (the grey powder), of position (the Brownian movement), and of density (the phenomenon of critical opalescence and the blue of the sky); the first are produced by the action of the mechanical agitation of the powder, the last two by the action of that no less complex agitation which is called "thermal agitation."

But this conception of fluctuations can be extended and generalized to many other magnitudes: fluctuations of temperature, fluctuations in the equipartition of energy, fluctuations of molecular velocities, fluctuations in the paramagnetic orientations of the molecules of a gas, fluctuations in chemical composition, fluctuations of dissociation, etc., etc.

In order to fix our ideas, let us consider the case of dissociation of iodine vapour under the action of temperature.

At a pressure of 40 cm. and a temperature of

1,300° C. it is found by the measurement of the density and Avogadro's law that the degree of dissociation is about 0·75; this means that "on the average" under these conditions 75 molecules out of every 100 are dissociated (that is, monatomic).

Let us translate this experimental fact into the language of the kinetic theories. Under the action of the molecular collisions resulting from the thermal agitation a certain number of diatomic molecules are dissociated each instant, whilst a certain number of dissociated molecules recombine on account of the accidental meëtings and become again diatomic.

The probability that at any instant all the molecules will be dissociated by the molecular impacts is, if not nil, at least very small; the probability that none will be dissociated is also almost nil. The proportion of 75 molecules dissociated out of every 100 which constitutes the equilibrium under the conditions of the experiment must correspond to the maximum probability. But this equilibrium is not invariable; it is a mobile equilibrium, characterized by the fact that at each instant there are approximately [1] as many molecules of iodine dissociating and becoming monatomic as there are dissociated molecules recombining. The degree of dissociation therefore varies at each instant because of this "approximately," and it is these oscillations round the most probable value that constitute the fluctuations of the dissociation for the state of equilibrium considered.

Examples like this could easily be multiplied.

[1] Sometimes more, sometimes less.

## 12. The limitations imposed on the second principle by fluctuations

This leads us to the consideration of the limitations which fluctuations impose on the second principle of thermodynamics.

We have seen that it can be assumed by virtue of that principle, that the physico-chemical phenomena which take place in the interior of an isolated system have the effect of making the system tend towards states which are more and more probable, so that the system attains a state of equilibrium when the probability of this state is a maximum in the analytical sense of the word.

Should this consequence of the second principle be considered as absolute ?

The phenomenon of fluctuations which we have just examined allows us to reply that this is not rigorously the case.

In fact, as we have just seen, at the moment of equilibrium the system is not in an invariable state, but on account of its fluctuations, it oscillates round a most probable value which is its theoretical equilibrium. It follows that the entropy, always proportional to the logarithm of the probability, will undergo oscillations which will remove it to a greater or less extent from its theoretical maximum value. Thus the entropy will have a " mean value " slightly smaller than that which corresponds exactly to the most probable value. When thermodynamics tells us that at the moment of equilibrium

the entropy is a maximum it does not take the fluctuations into account because it assumes them to be without practical importance, which it is permissible to do in the majority of cases. This does not make it less interesting to show that by reason of this fact the phenomenon of fluctuations imposes a first restriction on the second principle of thermodynamics.

But the restrictions which fluctuations are capable of imposing on the second principle can be much more serious.

In fact, it is possible to suppose that a fluctuation of large amplitude is able, theoretically at least, to make the system return to an anterior state, or even to its initial state ; thus making the entropy decrease, not only by quantities inaccessible to experiment, but making it proceed altogether in the reverse direction. This would then be the pure and simple negation of the second principle.

In paragraph (14) we shall discuss in more detail this possible return to the initial state, but we shall confine ourselves for the present to showing that the phenomenon of fluctuations removes, at least theoretically, the absolutely rigorous character which is usually accorded to the second principle of thermodynamics and to the numerous consequences which follow from it.

## 13. Fluctuations in biological phenomena

We have just seen that physicists have only succeeded with difficulty in detecting the pheno-

menon of fluctuations in laws which, at first sight, would have been thought to be absolutely precise.

As has been said, this difficulty arises principally from the prodigious number of elements (atoms, molecules, etc.) which are involved in the smallest physical phenomenon. The law of large numbers is generally satisfied with a precision which greatly exceeds the delicacy of our experimental methods of investigation.

The contrary is the most frequently the case when biological statistics are considered.

*The number of elements which are involved in statistics of this type is then incomparably more restricted and the amplitude of the fluctuations is such that they very often mask, at first sight, the general tendency, which is the statistical law.*

For example, suppose we desire to ascertain the ratio of the number of masculine births to the number of feminine births, and let us limit our inquiry to a single family taken at random in any country whatsoever; it will be impossible for us to arrive at an exact conclusion. Under these conditions, therefore, we can no more obtain the general law than we can deduce the law of the displacement of the particles in the Brownian movement by the observation of the trajectory of a single particle for a relatively short time.

In both cases it may be said that the fluctuation masks the general tendency.

But if we extend our inquiry to the whole of a country, or better still to several countries, we find that the ratio of masculine births to feminine births

is approximately the same everywhere and in the neighbourhood of 1·05.

| | | | |
|---|---|---|---|
| Norway | 1·056 | Wurtemburg | 1·043 |
| Russia in Europe | 1·05 | Baden | 1·049 |
| Denmark | 1·05 | Great Britain | 1·053 |
| Finland | 1·049 | Austria | 1·061 |
| Croatia, Slavonia | 1·058 | Switzerland | 1·052 |
| Russian Poland | 1·01 | Belgium | 1·047 |
| Roumania | 1·108 | Holland | 1·052 |
| Serbia | 1·058 | Italy | 1·063 |
| Prussia | 1·053 | Spain | 1·083 |
| Alsace-Lorraine | 1·051 | Greece | 1·138 |
| Bavaria | 1·052 | Portugal | 1·071 |
| Saxony | 1·05 | France | 1·047 |

To this difficulty arising from the more restricted number of the elements in biological statistics is to be added a second which is not less important: the uncertainty which is usually experienced of *the homogeneity of the biological material* on which the inquiry is carried out.

In fact, it is only by experimenting on an absolutely homogeneous material, or at least on one of well-defined homogeneity, that it will be possible to obtain really useful conclusions from the statistics.

Similarly it is in general more profitable to science to study the physical properties of a pure substance, a gas for example, than those of some badly defined mixture of all sorts of substances.

Whilst it is possible that this latter study will lead to interesting results, it is beyond doubt that the results of these experiments will be, if not

absolutely incapable of interpretation, at least extremely complicated.

But what is a homogeneous biological material and how can this homogeneity be recognized ?

In a general way it appears that the more the individuals to whom the statistics refer are related, that is to say the more alike they are by reason of heredity and the conditions under which they have developed, the easier it will be to arrive at a definite conclusion with a relatively restricted number of individuals ; the easier it will be also to interpret with security the results of the statistics.

Thus there would be more chance of being able to draw a useful conclusion from the statistics by working with selected races, raised under definite conditions (Chodat).

It is true that it has been objected to this method of investigation that the conditions of the laboratory are not those of nature, and that these laboratory statistics would not necessarily be applicable to the development of the same individuals if they were produced naturally. This is incontestable, but the conclusions from these simplified experiments do not the less permit, in general, the interpretation with more security of what actually happens in nature.

The biologist who experiments on carefully selected races under simplified conditions differing but little from those of nature is in the same position as the physicist who, desiring to know the laws of the atmosphere, commences by studying the laws

of gases under simpler conditions, with a smaller number of independent variables. He will study first their compressibility at constant temperature and will obtain Boyle-Mariotte's law; then he will experiment at constant pressure, the temperature being variable, and the result will be Gay-Lussac's law. In possession of these two laws, he will be in a better position to attack the study of the atmosphere and to interpret the phenomena which occur therein.

### *The interpretation of biological statistics*

Every one who possesses a little patience can compile statistics in any domain whatever. It is more difficult to do it under conditions such that the results can be interpreted, and in this connection we have just seen that by experimenting on pure lines, for example, the chances of arriving at a sound interpretation are considerably increased.

This interpretation remains a very delicate task, and the biologist will be the better able to perform it the more completely he knows the material on which the investigations have been carried out, the deeper his general knowledge of biology, the better his judgment, and the more he is possessed of a scientific mind.

But independently of these requirements, which are most essential and which it is almost commonplace to recall, biometry has placed at the disposition of its disciples quite a series of rules and of methods of calculation to facilitate the interpreta-

tion of biometric statistics and to permit the easier recognition of the general tendencies, the statistical laws.

Such are, for example, the methods for resolving any curve whatever into a certain number of symmetrical probability curves, and so on.

In order to bring out more clearly the analogies between these methods and the interpretation of experiments in physical-chemistry, a concrete example will be taken.

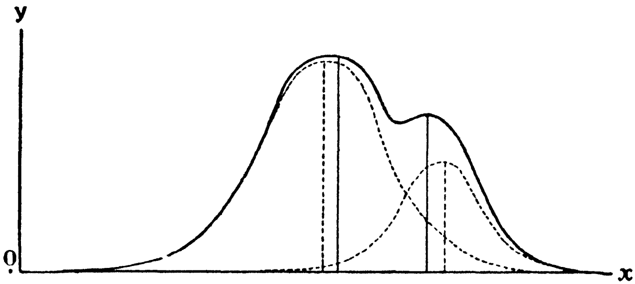


FIG. 4.

Let us suppose that statistics referring to a particular character (the height of an adult, for example) have been compiled from a group of 10,000 individuals, chosen haphazard from a very numerous biological material, and that the results are represented by the continuous curve in Fig. 4.

In this curve the abscissa $x$ represents the *height* measured, and the ordinate $y$ is what is called the *frequency*, or the number of individuals having exactly this height $x$.

Let us take from the same biological material a new group of 10,000 individuals, then a third, and so on, and construct similar curves of the distribution of height.

If these various curves approximately coincide, we conclude that the distribution of height for the material studied follows a general tendency which is independent of the individuals chosen, provided that the number measured is large enough and that they are chosen at random.

We could not conclude that the material is homogeneous, in the sense that it concerns a pure race; it might very well be composed of an intimate mixture of two or more species. The curve in Fig. 4, indeed, represents in this case the general tendency "for the mixture investigated," but it would be modified if the proportion of the two species in the mixture were varied. It might be said that in this case the material constitutes a *population*. The biologist will then be exactly in the position of the physicist who, by taking samples from a mixture of gases, shows that the properties of this mixture are independent of the place from which the sample is taken.

But we are concerned with interpreting the result represented in Fig. 4. For this purpose the biologist will endeavour, for example, to resolve the curve into two or more simpler distribution curves. Let us suppose that this analysis has permitted him to consider the curve with the double peak in Fig. 4 as the result of the superposition of two symmetrical probability curves (dotted curves); he

would then have recourse to his biological knowledge to interpret this result.

If he has reason to believe that his biological material is a mixture of two different species, one of smaller stature, the other of greater stature, it will seem natural to him to consider the curve on the left as representing the distribution of height for the first species, and that on the right as concerning the taller race.

The area comprised between each of our curves and the $x$ axis will give the number of individuals of each species, and consequently the proportion of the mixture. He would then be able to study other characters and see whether these conclusions were confirmed.

Let us remark, however, that a set of statistics can rarely be interpreted in such a simple manner as this. In particular, the biological material, "above all, if it is taken direct from nature," may very well contain, not only the two species, but in addition, if they are neighbouring species, the results of their crossings, and these products of crossings may or may not follow Mendel's law relative to the character investigated. It follows that the interpretation of the statistical curve may become extremely difficult. Finally, it is important to observe that such a material may behave, relative to one character, as a homogeneous material, and no longer do so with respect to another character. For example, by the investigation of such a character a very definite probability curve might be obtained, which would point to the existence of a pure race.

Then, passing to the statistical investigation of another character, using the same material, a double-peaked curve might be obtained, which would indicate the existence of two species, or at least of dimorphism.

It is therefore possible for the biologist to be exactly in the position of the physicist who studies the laws of the dilatation or of the compressibility of rarefied gases. It is immaterial to him on what gas he investigates these laws. Whether the gas be pure or whether it is a mixture of rarefied gases which have no chemical action on each other, the result will always be the same within certain limits; either Boyle-Mariotte's law or Gay-Lussac's law. This would no longer be the case if his investigation concerned the density or some other specific property.

Certain characters, therefore, may be imagined to be common to neighbouring species, and those characters, considered by themselves, might create the belief in the existence of a single species.

Finally, even when working with pure lines, the curve showing the distribution of the deviations is not necessarily symmetrical, and similar to a probability curve, whatever the character investigated. It is not apparent, in fact, why the increase of a character should always be as probable as its diminution. We have seen that in the domain of physics the distribution of the molecular velocities of a gas (Maxwell's law) is not symmetrical on either side of the most probable velocity; the probability of a given increase in the velocity is

not, therefore, equal to that of a diminution of the same magnitude.

*The significance of symmetrical probability curves*

What conclusions should be drawn when the statistical examination of a character leads to the representation of the deviations round the most probable value by a symmetrical probability curve ?

In order to reply to this question it is best to return to the theory of accidental errors which is considered in the calculus of probabilities.

In this connection it will be recalled that Gauss's law on the accidental errors can be proved from the following hypotheses (Poincaré) [1] : "*the actual error is the resultant of a very large number of partial and independent errors*" (or, which comes to the same thing, errors which are inter-related by laws whose effects are almost infinitely complex, such as those of mechanical or thermal agitation) ; "*all these partial errors are very small, and in addition each of them may obey any law of probability whatever, provided that the probability of a positive error is the same as that of an error equal to it and of opposite sign.*"

Let us try to apply these considerations to a concrete example ; and suppose that the symmetrical probability curve represents the distribution of the height of the adults in a certain country. We say then : whatever may be the complexity of the causes which have the effect of modifying the

[1] Science et Hypothèse, p. 241.

height of an individual, on the whole they tend to produce a type the height of which corresponds to the mean height,[1] in the same way as at the game of roulette the player tends to win one spin out of every two.

Further, we can suppose that a multitude of causes, independent of each other or related by extremely complex laws, all act so as to cause deviations from this mean height sometimes in one direction and sometimes in the other, the probability of a positive deviation being always the same as the probability of a negative deviation of the same amplitude. In the example which we have chosen these causes may be the quality or the quantity of the food, the manner of life, heredity, the climate, etc., etc.

Such is *the meaning which may be attached to symmetrical probability curves, but it is by no means proved that this is the only one.*

The formula $y = Ce^{-k^2x^2}$ may, in fact, be based on considerations quite different from those which have been adduced.

### *Psychological Statistics*

If, now, we pass from biological statistics to those compiled in the domain of psychology, the difficulties of a satisfactory interpretation increase further.

[1] This results from the fact that in symmetrical probability curves the most probable value coincides with the mean value on account of the symmetry of the curve about the maximum.

The individuals on whom this type of investigation are made are often very dissimilar, not only psychologically at the time of the experiment, but on account of the anterior conditions of their existence; the number which it is thought necessary to group together for the study of a particular character is often very small; their choice as well as the numerical evaluation of the character may be more or less arbitrary. It is therefore natural that under these conditions there is less hope of being able to draw a definite conclusion.

Nevertheless, if the deviations follow Gauss's law, it is permissible to apply the same general considerations to the results of these statistics as to those relating to physico-chemical or biological phenomena. It is still necessary, in order that this application may be justifiable, that the statistics should be based on a "very large number of cases." Otherwise the derivation of a probability curve will be simply a coincidence.

But whatever the difficulties inherent in the interpretation of psychological statistics, they can, nevertheless, be extremely useful. Very often they bring out interesting *correlations*, though they do not always explain them. Examples of this are to be found in the correlation between the form of the cranium and criminality; in the progressive increase in the number of errors which a calculator commits with the time which he has worked; and so on.

## 14. The consequences of an individual action on the molecules

(The hypothesis of Maxwell's demon)

When we have obtained a uniform grey powder by the agitation of two powders, black and white, what means have we at our disposal for reproducing the initial state, that is to say, for separating the black grains from the white grains ?

Actually, there are two methods.

The first consists in continuing the agitation till a fluctuation leads to some permutation which is equivalent to the initial state.

Unfortunately, this method is generally desperately long. In the case of only 20 grains this fluctuation would only occur, on the average, once in 184,756 agitations (see Table I, page 52). If the tube were shaken up once per second, it would take " on the average " not less than two days for the desired fluctuation to occur.

But when the powder is composed of a very much larger number of grains, as in the case of the molecules of two mixed gases, the thermal agitation would not have to proceed for days only, but probably for millions of centuries, in order that there might be a chance of the fluctuation in question being suddenly produced. This is as much as to say that we must give up hope of this miracle occurring.

The second method at our disposal for resolving the grey powder into its elements consists in sorting out

the grains of each colour, that is to say, in *exercising an individual action on every one of them.* This method can be employed if the grains are neither too small nor too numerous; we should not fail to use it in the case of our powder of 20 grains.

Unfortunately, this very simple method ceases to be of use when we penetrate into the region of molecular magnitudes.

We then have neither a sense sufficiently fine nor fingers sufficiently delicate to exercise an action of this type on the molecules individually. It is this incapacity, when we are concerned with isolated molecules, which is the cause of the evolution towards the most probable states, that is to say, in the direction indicated by the laws of chance, which always occurs in practice. It is this which makes us include among the principles which govern our experimental laws the second principle of thermodynamics, the exact significance of which has just been demonstrated.

But that which is impossible for us may be possible for other agents. Let us conceive a being sufficiently tenuous, able to pass in and out between the molecules and to act individually on each of them like Maxwell's demon, and the second principle of thermodynamics will not exist. This being will be able at will to cause our phenomena to proceed in a direction opposite to their probability; in the language of thermodynamics, he will be able to cause the entropy to diminish. In this way it would be possible for him to sort out and manipulate the molecules of a homogeneous mixture of gases

in such a way as to re-establish the original separation, to our great amazement.

Similarly, by acting on the molecules of a mass of tepid water he would be able to separate the molecules possessing a high velocity (hot molecules) from those having a lower velocity (cold molecules), and thus to obtain hot water and cold water, without any change in the total energy. By means of these two sources at different temperatures it would be possible for him to work a heat engine producing mechanical work according to the ordinary principles of our thermodynamics.

It follows that if we knew how to carry out this sorting out of hot molecules and cold molecules, transatlantic liners would no longer have to carry coal; the energy for their propulsion would be found in the ocean, which constitutes an enormous reservoir of molecular kinetic energy. This manipulation would permit us to obtain the two sources at different temperatures which are indispensable to the working of all heat engines.

In short, *it is our inability to co-ordinate molecular motion which renders almost useless to us the vast quantity of mechanical energy which it represents.*

### *A hypothesis on the action of certain catalysers*

But though we cannot act on the individual molecules, is it possible that there are agents endowed with this power ?

It has been sometimes questioned whether the mysterious action of certain catalysers may not have an origin of this nature. We have in the

catalyser, in fact, a substance which, merely by its presence and without appearing to participate at all in the reaction, plays a preponderating part therein, and multiplies its velocity to an extent which is often prodigious.

Let us suppose, for example, that the catalyser acts as a net and retains in its vicinity the molecules which have a high velocity. On this account there will be a relatively high proportion of such molecules in its immediate proximity. But these molecules with a large energy are particularly apt to produce the dislocations which must often precede the recombination of the substances present; the velocity of the reaction will therefore be considerably increased in the neighbourhood of the catalyser. This is obviously purely hypothetical, but it will be understood that in the presence of facts as singular as the action of catalysers this hypothesis has been added to all those which have been advanced to explain this mysterious *action by presence.*

### *The remark of Helmholtz on the vital principle* [1]

The hypothesis which Helmholtz advanced some time ago, and according to which the phenomena of life may very well escape, in part at least, from the second principle of thermodynamics, is also connected with a principle of individual action on the molecules.

Thus it must be assumed, according to this hypo-

[1] For the more complete study of this question, see the third paper.

thesis, that the vital principle is something particularly tenuous and capable of acting on the individual molecules after the manner of Maxwell's demon. To a certain extent, therefore, it will be able to cause phenomena to proceed in a direction opposite to that of the statistical probabilities which constitute our physico-chemical laws. *The vital equilibrium will be due then to the fact that the chemical reactions in the interior of the living organism will no longer necessarily follow the evolution which tends to make the system change to a more probable state.* Life will thus be like a struggle against the blind laws of chance.

At the death of the organism, the vital principle being exhausted or absent, our statistical laws will again resume their operations with the quasi-finality which characterizes them.

Such are the consequences of the hypothesis advanced by Helmholtz in the language of our present conceptions.

*This is evidently a very bold and gratuitous hypothesis*, but one which it is interesting to recall in the presence of the insoluble mysteries of life. Instead of proofs it has the fortune to be supported by the high scientific authority of Helmholtz.[1]

[1] It is scarcely necessary to say that almost insurmountable difficulties would be encountered in the verification of such a hypothesis. Not only would it be impossible practically to evaluate the entropy of a system as complex as a living organism, but this organism does not, by itself, constitute an isolated system. It would be necessary to include in the system investigated the medium with which, in practice, the organism effects its exchanges.

# THIRD PART

## THE STATISTICAL LAWS

### 15. Physico-chemical laws

To assert that a phenomenon is impossible or to declare that its chance of occurring is one in a hundred million is "practically" to say the same thing. It follows that the scientist, in the prosecution of his scientific research, will remain a convinced determinist, whether he considers the physico-chemical law to be an absolutely irrevocable decision or whether he adopts the new and larger ideas which have just been developed. In the latter case, however, his determinism will be less absolute; it will be a "statistical determinism" which may some day be overthrown, theoretically at least, by the miracle of a fluctuation of large amplitude.

Though there is no difference "from the practical point of view" between these two conceptions, it can be said, nevertheless, that they are separated by an abyss when looked at "from the philosophical point of view."

In fact, the new conception ceases to ascribe to the physico-chemical law, as we know it on our scale of observation, an inflexible and inevitable character, there being always the possibility of the occurrence of a fluctuation which would make our

universe evolve in a sense both unexpected and contrary to that assigned to it by our scientific forecasts.

But must we consider all our experimental laws as statistical laws more or less subject to fluctuations?

It does not appear that we have the right to consider them all in this way to the same extent. We can, it is true, consider as statistical laws all those in which we have been able to establish experimentally, if not fluctuations themselves, at least their immediate consequences. Such are, for example, the laws of gases; to these should probably be added all those which result from the very numerous kinetic theories of physical chemistry.

On the other hand, there is not the same rigorous necessity for the consideration of laws as statistical laws in other domains, and particularly in the case of universal gravitation.

Moreover, it does not appear that universal gravitation can be considered as a physico-chemical law. It has been established, in fact, that the weight of a substance is absolutely independent of the state of chemical aggregation of its atoms, and of their temperature; and the verification of this is probably one of the most precise which has been made [1] (the law of the conservation of mass).

[1] According to modern ideas, developed particularly by Einstein, gravitation must be considered as the attraction of energy by energy, every body containing an energy proportional to its inertia, or more exactly the energy of a body being equal to its inertia multiplied by the square

Fluctuations of gravity have never been established by experiment. It is true that we can always entrench ourselves behind the supposition that fluctuations exist but that they are masked by the law of large numbers.

In short, it cannot be asserted at the present time that all our experimental laws are statistical laws involving fluctuations, but the very nature of the modern ideas of the structure of matter and the considerable number of discontinuous elements which are involved in the smallest phenomenon does not exclude this possibility, and even makes it very probable, at least so far as physico-chemical laws are concerned.

## 16. Molecular, atomic, and electronic laws

We have just seen that the laws of physical chemistry can be considered as being very probably statistical laws. One of the particular consequences

of the velocity of light. From this point of view, the inertia of a body must be slightly greater when it is hot than when it is cold, but by an amount which is experimentally inappreciable. Similarly, when bodies attain considerable velocities (cathode rays) the enormous kinetic energy which they acquire should result in an increase in their coefficient of inertia. This increase has been experimentally established in the case of the high-velocity cathode rays and the $\beta$ rays of radium. In this connection see C. E. Guye et C. Lavanchy, *Vérification expérimentale de la formule de Lorentz-Einstein*, Comptes Rendus, July, 1915, and Arch. de Genève, October, November, and December, 1916.

of this conception—and it is not the least interesting—is that it leaves the laws of the individual actions between molecules, atoms, or electrons completely undetermined.

What can be the nature of these laws? Must they be considered as inflexible laws, or are they statistical laws of still smaller hypothetical elements?

Finally, "in the presence of this uncertainty," it is permissible to ask—and the question sometimes has been asked—whether all or some of the molecules or atoms may not be endowed with free will, without our physico-chemical laws being sensibly modified thereby.

We shall not attempt to reply to this question. That would be to go outside the limits which we have imposed on ourselves in this paper and at the same time to penetrate into a region which is particularly difficult and where the aid of experiment is almost completely unavailable.

From the experimental point of view, in fact, we know very little about the laws which may govern the actions between two atoms, two molecules, or two electrons; almost all our experiments call into play millions of millions of molecules; thus they only give us the collective laws which, in a general way, we call "physico-chemical laws."

Some rare experiments, however, that with the spinthariscope, for example, cause us to witness the actions which individual molecules can exert. In this curious experiment it seems probable that each $\alpha$ particle (or charged helium atom), when projected

by a radioactive substance against a phosphorescent screen, gives rise to a kind of flash, like that produced by the explosion of a projectile on striking its target. Thus, by counting the flashes, the number of helium atoms produced by the decomposition of the radioactive substance in a given time can be obtained. In this way the experiment enables us to form an idea of the length of the "life" of the substance.

In this connection must be mentioned the remarkable experiments by which C. T. R. Wilson, using the phenomena of the condensation of saturated vapours, has been able to make visible, and even to photograph, the trajectories of these atomic projectiles. The photographs which have been obtained clearly show the paths, which are at first rectilinear and then bend in an irregular manner near the end of their course. It appears that when the atomic projectile has lost sufficient kinetic energy, it makes a series of ricochets before it is finally arrested.

We may also hope to obtain some information concerning the actions between individual atoms or molecules by means of the ultramicroscope. In fact, with this arrangement it is possible to make visible particles which are of the same order of magnitude as the largest molecules in organic chemistry. Recent investigations on X-ray spectra are giving us information concerning the disposition and the symmetry in the position of the atoms in solid bodies.

Finally, by means of observations on the fall of electrified spheres, Millikan has found it possible

to experiment on individual electrons and to determine, not their mean charge, but their actual charge ; it is known that, within the limits of the errors of experiments which are already very accurate, this charge is the same for all electrons.

In brief, although there is as yet little experimental information available concerning the action of molecule on molecule, atom on atom, or of electron on electron, there is, nevertheless, hope that it will increase.

But, without attempting in any way to forecast the nature of the laws which may govern the interaction of molecules or atoms, it may be useful to recall that statistical laws (such as our physico-chemical laws) are not incompatible with a rigorous determinism.

For example,[1] let us take the first 10,000 logarithms in mathematical tables to ten decimal places and let us compile statistics of all the figures which occupy the seventh place. We find that the zero appears 990 times ; the figure 1, 997 times ; the 2, 993 times ; the 4, 1,012 times ; and so on. In other words, the number of appearances of each of these figures (including zero) is approximately the same as if the figures had been drawn at random from an urn which contained equal numbers of them all.

Further, if the 10,000 logarithms are divided into 10 series of 1,000 each and the same statistics are

[1] Bertrand, *Calcul des probabilités*, Preface ; Carvallo, *Le calcul des probabilités et ses applications*.

compiled for each of these series, it is found that the frequency of each figure (including zero) is about 100, but that there is a deviation. The ten series, therefore, give ten deviations for each figure, or 100 deviations in all. The curve showing the distribution of the deviations is very approximately a symmetrical probability curve, closely corresponding to the formula $y = Ce^{-k^2x^2}$.

Thus we have a statistical law resulting from a perfectly clear and precise relation. *In fact, there is nothing more definite than the interdependence of a number and its logarithm.* It may be concluded, therefore, that statistical laws are not incompatible with a rigorous determinism.

In this determinist conception, then, what we call "chance" is the consequence of causes which are perfectly definite and which may be simple, but the combined effects of which may become so complex that we are unable to calculate them. We then call upon statistics to reveal them to us. It may be said that from this point of view "the calculus of probabilities and Bernoulli's law are capable of embracing all the domains of human activity."[1]

In short, *the very probable hypothesis of statistical physico-chemical laws does not exclude that of a rigorous determinism; but if this absolute determinism exists it is relegated into the region, which is almost unknown experimentally, of the individual actions between atoms, molecules, and electrons.*

What will be the case when these actions are

[1] Carvallo, *loc. cit.*, p. 39.

better known? Will absolute determinism then take refuge in an infinitely small quantity of another order of smallness, and so on?

## 17. Intra-atomic laws

It has been said in the preceding paragraph that we know very little about the actions which individual atoms and molecules can exert on each other. There is more information concerning what happens at the surface or in the interior of the atoms.

This world has been opened to our investigations principally by two different means. On the one hand, the spectroscope, by the analysis of the light emitted, tells us about the nature of the motions of the electric charges which enter into the constitution of the atoms. On the other hand, the discovery and the study of radioactive substances has thrown some light on the laws of the disintegration or the destruction of the atomic edifices.

Although we are only at the dawn of the discoveries which the intra-atomic world holds in store for us, one important fact seems already clearly to have emerged: this is *the extreme complexity* which must be presented in the majority of cases by this "microcosm" which is called the atom. A first proof of this complexity is furnished by the observation of spectra. It is known, in fact, that the spectra even of chemical elements sometimes reveal an astonishing variety of periodic movements, probably due to the oscillations of the electrons which enter into the constitution of the atoms. The

number of spectral lines which correspond to them is often very great: it is known that the iron atom can emit several thousands of spectral lines, to which it would seem that there should correspond as many different vibratory motions, or at least as many components of different period.

It is true that these periodic motions have sometimes been correlated between themselves (Balmer's and analogous formulæ), and that certain groups of spectral lines are subject to the same modifications depending on the conditions of the experiment. In addition, it is permissible to question whether the multiplicity of spectral lines characteristic of an element is indeed due to periodic motions taking place simultaneously in the interior of the same atom. May they not correspond to the various phases through which an atom passes, successively, under definite conditions? This idea has been advanced. The simultaneous appearance of the various lines would then be due to the large number of atoms called into play in the experiment, or to the very rapid succession of these phases.

Whether these motions be successive or simultaneous, the complexity which gives rise to the possibility of so many different vibratory motions does none the less exist.

But the complexity of the atom is indicated, above all, by the law of the disintegration of radioactive substances.

It is well known that this law is represented by a negative exponential, that is to say, by an expres-

sion which "bears the mark of chance," the external sign of a statistical law (Debierne).

This point especially deserves our attention because it appears probable that in this case the complexity whence results the very form of the law of disintegration is right in the inside of the atom.[1]

[1] In order to show that the *laws of radioactivity can be statistical laws*, they should be compared with the law of monomolecular chemical reactions. This latter law is represented, as is the law of disintegration, by a negative exponential; it may be interpreted as follows:

Under the action of the thermal agitation all the molecules collide with one another, and it can be assumed that, on account of the disorder and complexity of these collisions, *the probability of the dislocation of a molecule is the same for all the molecules.* Thus the number of molecules broken up in a given time will be proportional to the total number $n$ of the molecules (law of mass).

Hence

$$-dn = an\,dt$$

whence

$$n = N_0 e^{-at}.$$

In radioactive phenomena the law of decay is also a negative exponential of the same form. But the disorder which results from thermal agitation can scarcely be considered to be the cause of the disintegration of atoms *since the temperature has no effect on the rate of decay.* Thus it is necessary to look for another disorder, another complexity, which must be, therefore, in the interior of the atom; either the atom may be considered to be composed of a considerable number of smaller elements or it may be supposed to possess a simpler structure by assuming that the various atoms exist in all the possible

This complexity may be attributed to the presence in the atom of a very large number of hypothetical smaller elements, but it can also be supposed that the atom is composed of only a small number of elements (like the planets of our solar system). The complexity would then arise from the fact that the systems corresponding to the different atoms might be in all the possible phases of their evolution, so that at every instant there would be a certain number which, arriving at an unstable state, would disintegrate, giving rise to the emission of $\alpha$, $\beta$, or $\gamma$ rays. This idea seems to prevail at the present time.

In short, *the very form of the laws of disintegration of radioactive substances is such as to give rise to the assumption that statistical laws also hold in the interior of the atom.*

But if the intra-atomic world which is revealed to us by radioactivity is probably very complex, it has the characteristic that it is almost closed to our physico-chemical agents, even to the most powerful of them.

In fact, though we are able to prove the disintegration of atoms by the laws of radioactivity, we

phases of their evolution. The fact that the probability of the explosion of an atom is the same for all atoms would follow from this complexity; whence the exponential law. In this connection see, among others, P. A. Guye, J. Ch. phys., p. 294 (1908), and Debierne, Conférence sur les transformations radioactives faite en 1912, *Les idées modernes sur la constitution de la matière*, Paris, Gauthier-Villars, p. 304 (1913).

have not as yet any agent capable of appreciably modifying this disintegration. Whatever chemical compound is formed by the radioactive atom, and even though it be raised to a temperature of 1,400° or lowered to a temperature of − 190°, the law of disintegration is unaltered and all the attempts hitherto made to modify it have proved to be in vain.

Thus the interior of the atom seems to be a closed world to us, and Poincaré tells us that "it is because it is guarded by severe keepers that the atom is an individual."

So far as the world of infinitely small intra-atomic things is concerned, therefore, we are spectators, just as our astronomers are spectators in the presence of the infinitely great in stellar space.

## CONCLUSIONS

From the foregoing considerations it will be seen that the conception of statistical laws tends to become generalized, and we need not be afraid to acknowledge that this is due to our ignorance and to our inability to penetrate the almost inextricable complexity of the smallest phenomenon.

Statistical laws, which for a long time seemed to apply exclusively to the *biological, social, economic, and kindred sciences*—precisely on account of the extreme complexity of the phenomena in these sciences, and because of the impossibility generally experienced of discerning the causes which produced them and made them vary—have been extended, little by little, by means of the calculus of probabilities to what are usually termed the "exact

sciences." It seems as though these latter sciences, and particularly physical chemistry, only owe their title of exact sciences to the law of large numbers, which usually renders the effects of fluctuations inappreciable.

In recent years these statistical laws have been introduced with particular intensity into *physical chemistry*, following the conception of the granular structure of matter and the generalization of the kinetic theories. Thus even the study of fluctuations and of their consequences has given to these theoretical conceptions a reality which may be termed experimental.

Briefly, the whole of the foregoing considerations show how the significance of our experimental laws tends to become profoundly modified. The tendency is to replace the physico-chemical law, which we have been accustomed to regard as final and inevitable, by the statistical law, which, theoretically at least, is liable to very rare exceptions.

*Thus this new conception tends to replace the absolute determinism of the laws of physics and chemistry, as we observe them, by a kind of larger statistical determinism.*

It is conceivable that equally essential modifications of the significance of even our experimental laws may some day or other have a profound effect on the evolution of philosophic thought.

# CARNOT'S PRINCIPLE AND THE PHYSICO-CHEMICAL EVOLUTION OF LIVING ORGANISMS [1]

## INTRODUCTION

THE conception of Carnot's principle as a line of demarcation between physico-chemical phenomena and vital phenomena is not new. It was fortunate enough to be advanced in the first place by the illustrious physicist Helmholtz, who, however, confined himself to a single remark, in a note to one of his papers on thermodynamics.[2] Since then this hypothesis has been reconsidered and considerably developed by various authors in publications which are mostly of a philosophical nature. It is also found in substance in Bergson's *Evolution Créatrice*, which shows us the vital spark everywhere tending to oppose the physico-chemical evolution which results from Carnot's principle.

[1] The ideas advanced in this article were the subject of a lecture at the Institut National Genevois, December 16, 1919. It has been thought best to give them here in a slightly extended form.

[2] *Gesamtabhandlungen*, II, p. 972. On this subject see the *Supplementary Note* at the end of this book.

The way in which physicists have regarded this principle since the researches of Gibbs and Boltzmann seems to us to have created a new interest in this question by permitting a more precise statement of its significance.

But before discussing this new point of view it will be well to recall briefly some of the principal arguments which have sometimes been advanced in favour of a vital physico-chemical evolution taking place in opposition or even in contradiction to Carnot's principle.

In the first part of this paper the point of view of classical thermodynamics will be exclusively adopted, reserving to the second part the examination of the question in the light of the modern conceptions which endow Carnot's principle with a new and less absolute significance. Finally, in the third part, several pages will be devoted to a short examination of the *philosophical aspect* of the new conception of Carnot's principle.

## FIRST PART

### THE POINT OF VIEW OF CLASSICAL THERMODYNAMICS

If Carnot's principle be considered as an *absolute principle,* there is no scientific reason for supposing that it should not be applicable to the physical chemistry of living organisms. This is what we shall endeavour to show in the first part.

Let us consider first some of the arguments which

have sometimes been advanced with the object of invalidating this principle.

### 1. *The high efficiency of the human machine*

It has been said that the high efficiency of the human machine as compared with heat engines renders Carnot's principle invalid.

Old investigations, confirmed by more recent experiments carried out in England and America,[1] have shown, in fact, that the human machine is capable of transforming into mechanical energy 21 per cent. of the chemical energy of the reactions of nutrition and respiration. It has been justly concluded that "if the human machine is a heat engine obeying the laws of thermodynamics," two sources of heat at very different temperatures must exist in some part of the organism or in the surrounding medium.

In the case of an efficiency of only 20 per cent. these temperatures must be + 115° C. and + 37·5° C., if the human body be considered to be at the temperature of the cold source; + 37·5° C. and − 24·6° C. if the body be considered as the hot source.[2] But such differences of temperature are

[1] Revue Générale des Sciences, October, 1908.

[2] It is known that the *maximum* efficiency of a heat engine only depends on the temperatures between which it works: this maximum efficiency is attained when the engine works through Carnot's cycle. In this case, it has the value $\eta = \frac{T_1 - T_2}{T_1}$, $T_1$ and $T_2$ being the absolute

nowhere to be found, either in the organism or in the surrounding medium. Moreover, it is very improbable that such different temperatures could exist in parts of the body so close together as to make their observation impossible.

In all probability, therefore, the human machine does not function as a heat engine ; that is to say, the chemical energy of the reactions of respiration and nutrition is not transformed into heat which is subsequently converted into mechanical work, by the operation, for example, of the phenomena of expansion, vaporization, and so on, taking place in the muscular tissue.

Besides, such a process would be particularly inefficient, and it would be very singular if nature chose for the production of mechanical energy in living beings precisely the most uneconomical method.

But the fact that the human machine does not function as a heat engine does not at all imply that the physico-chemical evolution in the interior of the living organism is in contradiction to Carnot's principle. In fact, the chemical energy of respiration and nutrition may be transformed into mechanical energy otherwise than by the intermediary of heat.

temperatures of the two sources. If the temperatures are expressed in degrees Centigrade, we have $\eta = \frac{t_1 - t_2}{t_1 + 273}$. The temperatures $+ 115°$ C. and $- 24{\cdot}6°$ C. are obtained by making $\eta = 0{\cdot}20$ in this latter relation, in the two cases.

Various hypotheses have been suggested, and among others one of the most attractive, at least for physicists, consists in regarding the capillary or electro-capillary phenomena taking place in the muscular tissue as the organ of this direct transformation of chemical energy into mechanical energy. The cellular and finely vascular structure of the tissues would appear to be in favour of a hypothesis of this kind, although the exact nature of the action cannot be stated.

In other words, the chemical actions taking place in the muscle would have the effect of modifying the nature of the surfaces of contact of the various media which constitute the muscular tissue. These variations of the capillary constants, analogous to those observed in electrolytic polarization, would in their turn involve the deformations which characterize muscular contraction, and so mechanical work would be produced.

Such is, in essentials and in outline, the very ingenious directing idea of the theory of d'Arsonval on muscular contraction. It is not for us to discuss it from the biological point of view, but it will be sufficient to observe that the efficiency of transformations of this nature may be incomparably greater than those of the best heat engines, and theoretically quite compatible with the observed efficiencies of the human machine. [1]

[1] According to Chauveau, chemical energy would be directly transformed into mechanical energy by the intervention of the phenomena of osmosis with an efficiency

In short, it is apparent that it is possible to conceive physico-chemical processes apart from thermal processes, compatible with the high mechanical efficiency of the human organism, without these being in contradiction to Carnot's principle.

In conclusion, it may be said:

*The high efficiency of the human machine in no way proves that this machine functions contrary to Carnot's principle; it only proves that it is probably not a thermal machine.*[1]

### 2. *The assumed struggle of living organisms against the degradation of energy*

It is known that the degradation of energy is a consequence of Carnot's principle; that is to say, this principle has the effect of making the quantity of energy transformable into mechanical work continually diminish. From this point of view, therefore, it can be considered as a *fatal principle* in the sense that it would slowly lead our universe towards equality of temperature and towards what is called, *on our scale*, immobility.

We ask ourselves, therefore, whether some corrective to this fatal consequence does not exist,

which might be very high. We wish to mention this theory, which appears to us to penetrate more profoundly still into the intimate mechanism of muscular contraction.

[1] I have no doubt that this last conclusion is actually admitted by the physiologists, though the deplorable habit of comparing the human machine to a steam engine, which transforms the chemical energy of coal into mechanical energy, still exists.

and sometimes it has been thought that this has been found in the phenomena of which the living organisms are the seat. May not the mission of living organisms, it has been asked, be to prevent this fatal degradation of energy and to struggle against this progressive diminution of the reserves of mechanical energy ? Physicists and philosophers are therefore eager to investigate by what means living organisms may be capable of accomplishing this mission.

But however suggestive the considerations which have been invoked in support of this idea, it must be recognized that their scientific basis is very fragile. This can easily be shown by some examples.

*Example* 1. One of the principal arguments advanced is the energy accumulated by plants at the surface of our earth.

In plants it is known that in the presence of chlorophyll solar energy gives rise to endothermic reactions, that is to say, to reactions which store up energy in the potential state. If plant life did not exist on the surface of our earth, it has been said, this solar energy, instead of being stored up in plants and later in the coal measures, would be degraded rapidly. That is to say, that after it had slightly raised the temperature of the earth's crust it would be dissipated without delay by radiation into space, by virtue of Carnot's principle. It appears, indeed, that by storing up this energy the presence of plant life has the effect of striving against the degradation of energy, if, indeed, this is not its ultimate object.

But, without discussing the part which may be played in this connection by living organisms and particularly by plants, it must be remarked that *purely physico-chemical processes can also retard this degradation of energy to a large extent.* Such a process, for example, is the evaporation which occurs at the surface of the oceans. If the surface of the oceans were covered with a layer of oil, evaporation would be inappreciable and the heat received would be degraded rapidly by being radiated into space in the state of "dark heat."

On the contrary, evaporation causes the water to be raised into the atmosphere at the expense of solar energy, to fall subsequently in the form of rain, giving rise to watercourses which are capable of producing mechanical work. In this way evaporation struggles against an immediate degradation of energy just like plant organisms.

If, then, it is desired to speak of a striving against the degradation of energy, it would be wrong to attribute to the vital processes an exclusive monopoly of the struggle, since, as we have just seen, it is possible to conceive physico-chemical processes which are more or less efficient in this respect, although it is impossible to establish exactly their relative efficacy.[1]

[1] In fact, it is difficult to ascertain to what extent evaporation can retard the degradation of energy. We know that it gives rise to watercourses and that it is thus capable of transforming annually a large quantity of solar energy into mechanical energy. But if there were no other intervention this mechanical energy would be degraded, in its

*Example* 2. Let us take our second example from the animal kingdom. We have just seen that the mechanical energy of watercourses is degraded without delay by being transformed almost entirely into heat. But the genius of man intervenes and he places turbines and dynamos in the path of the moving water and thus part of the energy of fall is stored in reserve, for example, by the manufacture of explosives, the mechanical power of which can be used later, at any desired time. It may be said that man, by his intervention, seems to have the power of striving against the degradation of energy.

turn, without delay by being converted almost entirely into heat—the kinetic energy of the watercourses being dissipated to a large extent on account of the viscosity of the water and on account of its friction against the earth.

Thus evaporation only seems to have retarded the degradation of energy. But this retardation is perhaps more considerable than is imagined, because in order to evaluate it, it would be necessary to know the mean duration of the sojourn of the water vapour in the atmosphere, from the moment when it is taken from the liquid surface of the ocean until the time when special circumstances allow it to be resolved into rain. The atmosphere, in fact, is like an immense reservoir of water vapour which is supplied by evaporation, and which only occasions atmospheric precipitations when it is too full, i.e. when it is in a state of supersaturation.

It is therefore rather difficult to ascertain in what measure this purely physico-chemical process retards the degradation of energy and what is its importance relative to that which is attributed to plants in this presumed struggle against the degradation of energy.

To that it may be rightly objected that, if the psychism of man permits him to strive against the degradation of energy by storing up the energies of nature, it permits him none the less easily to precipitate this degradation. Does not the wastage of the coal measures which characterizes civilization accelerate this degradation in a particularly disquieting manner ?

If we had to formulate a conclusion on this subject we should be rather inclined to suppose, with Dastre and other authors, that the presence of vegetation has the effect of storing up slowly the reserves of energy, partly to the profit of the animals which have the ability to use them, and even to degrade them in what is sometimes an extremely short time.

This conception has at least the advantage of showing that there must be established on the one hand an equilibrium between the living organisms of the two kingdoms, and on the other a struggle between the different species of animals for the monopoly of this undegraded energy which is essential to their existence.

But let us leave this question, which takes us very far from our subject, and which, moreover, is not the one which interests us.

In short, it may be seen from these examples how easy it is to argue for or against this hypothesis of a struggle of life against the degradation of energy. In addition, as none of these pretended scientific arguments can be submitted to the test of a rigorous verification, it is conceivable that they might easily

be multiplied and that they must be considered, not as proofs, but simply as speculations, the scientific value of which is more apparent than real.

### 3. *Have living organisms the ability to use intra-atomic energy?*

This hypothesis is altogether gratuitous, but it is suggested by the discovery of radioactive substances which are known to be capable of liberating an enormous quantity of energy without an appreciable loss of weight.

If living beings had the ability to use intra-atomic energy, it would follow that their physiology apparently would not conform to the principle of the conservation of energy, at least in the form in which it has been conceived in physical chemistry hitherto. In other words, the utilization of intra-atomic energy by the living being would give it every appearance of being a creator of energy.

But in order that this hypothesis should have any value it would be necessary to prove that the energy expended in various ways by the animal is greater than that which corresponds to the combustion of the food which it ingests.

Let us suppose, for example, that the progress of experimental aerodynamics permitted us to evaluate accurately the minimum mechanical work developed by the flight of a swallow during the hours which it daily devotes to this exercise; and let us add to this energy the loss of heat energy by radiation and convection, which loss must be

very considerable since the temperature of the bird (42° C.) is generally very much higher than that of the surrounding medium. On the other hand, by means of the bomb calorimeter, we might be able to evaluate the heat of combustion of the daily ration of mosquitos, flies, etc., which constitute the diet of the swallow and which it catches in its flight. If a further small correction were made for the residual calorific power of the daily excretions, we should have the principal elements for compiling an approximate, if not an exact, balance sheet of energy. If the energy expended were *very appreciably* greater than the energy received, there would be reason to have recourse to the hypothesis of a utilization of intra-atomic energy by the animal.

The example of the swallow has been chosen because it does not seem, at first sight, that the ingestion of a mosquito can provide for the expenditure of numerous strokes of the wing and for the corresponding maintenance of the temperature of the bird.

But appearances may be very deceiving. The flight of the swallow may, in fact, necessitate much less energy than we suppose, because we do not know to what extent the bird can utilize the energy of the wind in its flight, nor exactly in what manner its plumage protects it against the loss of heat.

Too many elements are lacking for the question to be decided in either way, and until there is proof to the contrary we must consider the hypothesis of the utilization of intra-atomic energy by living beings as absolutely gratuitous. We shall not dwell

on this further, therefore, more especially as experiments carried out in America on man have led to an almost exact balance sheet.

4. *Do there exist physico-chemical processes which are capable of causing a diminution in the entropy of the system which includes them?*

When we spoke of the presumed struggle of living organisms against the degradation of energy, we said that certain processes, the growth of plants, for example, could have the effect of *retarding* the degradation of energy.

We are not concerned, however, with ascertaining whether living, catalytic, or other processes, are capable of retarding, to a greater or less extent, the degradation of energy, but we wish to investigate whether these processes are or are not in contradiction to Carnot's principle; for example, we desire to know whether these processes can cause a diminution in the entropy of the system which includes them.

If such were the case, it would be possible to conceive that a living being, such as a fish, might be able to co-ordinate to its profit the motion due to the thermal agitation of the water in which it swims in order to transform it into directed mechanical energy, thus realizing, contrary to Carnot's principle, a thermal machine functioning with only one source of heat; the fish having sensibly the same temperature as the water.

In order that what follows may be understood,

it may be useful first to illustrate by an example the fundamental distinction which exists between a process which has the effect of *retarding the increase* of the entropy of an isolated system and a process which, in flagrant contradiction to Carnot's principle, at least so far as it is considered from the point of view of classical thermodynamics, may occasion a diminution of this entropy.

Let us suppose that we have two different gases (hydrogen and oxygen) at the same pressure and the same temperature, and initially separated. It is known that when these two gaseous masses are mixed by diffusion the entropy of the system increases, in accordance with Carnot's principle. But let us suppose that instead of allowing diffusion to take place freely the two gases are separated by a porous partition which has no chemical action on either of them; this partition will have the effect of opposing the diffusion and of *retarding* the increase of entropy, and in this there is nothing contrary to Carnot's principle.

On the other hand, let us suppose for a moment that, when the mixture has taken place, it were possible to find a dissymmetric diaphragm which would only allow the passage of high-speed molecules (hydrogen) *in one direction* and of low-speed molecules (oxygen) *in the opposite direction.* This mysterious diaphragm would have the property of reproducing the initial separation of the two gases without the supply of additional energy; it would succeed in diminishing the entropy of the system *by its presence alone,* and thus would play a

part analogous to that of Maxwell's metaphysical demon.

But *at present we do not know of any physico-chemical process, catalytic or otherwise, which possesses the power to cause the entropy of a system to assume a lower value under these conditions.*

So far as we know, none of the arrangements which have been tried or conceived with a view to invalidating Carnot's principle, as it results from classical thermodynamics, have withstood a searching critical examination. In particular, such is the case with one of the most ingenious, namely, the separation of the hot molecules from a gaseous mixture by a gravitational field. Professor Berthoud [1] has shown recently in a minute critical examination that this separation also involves an increase in the entropy if the change in the volume which accompanies the separation is taken into account.

Therefore, until we have proof to the contrary, we must suppose that all the known processes can only retard the increase of entropy. This is the conclusion which must be drawn at the present time, at least if the question is examined solely from the point of view of classical thermodynamics.

### 5. *Conclusions from the first part*

If Carnot's principle be regarded as an absolute principle in inorganic evolution, there is no scien-

[1] Berthoud, Jour. de Chimie Physique, 1919, **17**, pp. 616 *et seq.*

tific reason for supposing that this principle is not applicable to the physico-chemical evolution of living organisms.

1. The high efficiency of the human machine does not at all invalidate Carnot's principle, it only proves that in all probability this machine is not a thermal machine.

2. The fact that the presence of living organisms, and particularly the presence of plants, is more advantageous for the retardation of the degradation of energy than the pure and simple heating of the earth's crust by the radiation from the sun, does not imply any contradiction to Carnot's principle, any more than does the evaporation which occurs at the surface of the oceans, which also seems to retard this degradation of energy. If plants do accumulate potential energy it is at the expense of the energy of the ultra-violet light and of the infra-red radiations of short wave-length which reaches them from the sun. In this transformation, however, this energy is partially degraded into long wave-length energy of less thermodynamical value. Nothing authorizes us to suppose that finally and on the whole the operation does not result in an increase of entropy in accordance with Carnot's principle.

3. As yet we do not know of any physico-chemical process, catalytic or otherwise, which is capable of causing a diminution in the entropy of an isolated system in which it takes place.

Finally, therefore, it is apparent that, if Carnot's principle is considered from the point of view of

classical thermodynamics, nothing authorizes us to suppose that it is limited to the physico-chemical evolution of the inorganic world. For this reason, it is not surprising that a number of brilliant men of science have accepted the generality of this principle which thus governs absolutely the evolution of living organisms as well as the world of inorganic matter.

Nevertheless, it is impossible not to be struck by the considerable differences which exist between vital physico-chemical evolution and the evolution of our reactions *in vitro*, by means of which Carnot's principle has been established.

In the first place, there is quite a collection of properties on which it would be almost commonplace to insist, and which together serve in some way to define living matter.

It will be sufficient to recall our inability experimentally to produce life otherwise than by means of life itself; the very complex phenomena which accompany the birth, the development, the reproduction, and the death of living beings; the tendency of life always to extend itself when the elements of the surrounding medium afford the possibility; the judicious exchanges which characterize assimilation; the adaptations which have all the appearance of intelligence and which go so far, for example, as to construct, with a remarkable exactness, an optical instrument in the womb of a living organism; in short, *the will to live, apparent or real*, which is found from one end to the other of the scale of living beings, and which, rightly or

wrongly, gives all the appearance of finalism to vital evolution. Finally, in order to make all this marvellous collection disappear, it is sufficient to shake slightly the molecular edifices by thermal agitation, by raising the temperature of the organisms a little above 100° Centigrade.

There is here quite a collection of facts which makes us think that in vital physico-chemical evolution there is something which, if it is not totally different from, is at least more complicated or *more general* than what we observe in the inanimate world.

# SECOND PART

## THE POINT OF VIEW OF STATISTICAL THERMODYNAMICS

We have just seen that if Carnot's principle be considered as an absolute principle, there is no scientific reason for supposing that it is not applicable to the physico-chemical evolution of living organisms.

Let us consider now how this conclusion is modified by the new conception of this principle.

### 1. *The modern conception of Carnot's principle*

In the first place, let us recall that Carnot's principle is nowadays considered as a statistical principle. If all the conclusions that are drawn

concerning the evolution of physico-chemical phenomena have the appearance of being absolutely certain, it is only because of the law of large numbers. This physico-chemical evolution, precise and definite as it seems, is in reality only the advance towards those disorders which are the most probable of all the possible disorders. In fact, it allows us to remain ignorant of the actions which molecules, atoms, or electrons can exercise between themselves, in order to arrive at only the statistical result of the whole, which we call a physico-chemical law.

This modern conception of Carnot's principle has been developed elsewhere,[1] and it was illustrated by an example which will be recalled very briefly here.

When a collection of an equal number of black and white grains is shaken up, a grey powder is always obtained if the agitation has been sufficiently prolonged. The result is "almost" inevitable, because of all the possible disorders, those which produce this grey impression on our eyes are very much the most numerous. This almost inevitable evolution towards the grey powder gives a very clear image of physico-chemical evolution according to Carnot's principle.

But if it is desired to fight against this statistical law, which tends to produce the grey powder, there are two methods available.

[1] J. de Chim. Phys., **15**, pp. 215–272. The evolution of physico-chemical phenomena and the calculus of probabilities (also Essay number 2 in this volume).

*The first* consists in acting on each grain individually. For example, by sorting them out one by one it would be possible to reproduce the initial separation into two kinds of grains, and in this way the statistical law of agitation could be overcome. In a mixture of gases this would be accomplished by Maxwell's metaphysical demon, which, so far as physico-chemical evolution is concerned, has been justly likened to a "cheat."

Similarly, it may be supposed that in living organisms there is a special agent (a true Maxwell's demon), and that this agent, which can be called the vital principle if desired, is something sufficiently attenuated to be capable of acting on the molecules individually. It would follow that in the interior of living organisms, physico-chemical evolution would no longer necessarily proceed towards the most probable states, as Carnot's principle requires, and that we should thus have a different physico-chemical evolution in living beings.[1]

Such a conception would naturally lead to dualist philosophies, but from the strictly scientific point of view it has the disadvantage of introducing, in the vital principle, an element which is distinctly metaphysical. Thus it would be out of place to dwell on it at length in this review.

*The second method* available for striving against the statistical law which tends to produce the grey powder consists purely and simply in prolonging

[1] This hypothesis has been mentioned already. J. de Chim. Phys., *loc. cit.* (page 102 of Essay number 2).

the agitation till *a fluctuation of a very rare type* leads to the initial separation. As Herodotus has said: "If one is sufficiently lavish with time, everything possible happens."

But this method is desperately long even if the powder is composed of a very small number of grains. It becomes, if not a theoretical, at least a "practical" impossibility when it is endeavoured to apply it to a system composed of innumerable molecules; and it is known that this practical impossibility gives rise to Carnot's principle as it is at present conceived. In virtue of this principle thermal agitation is practically unable to separate two gases once they are mixed. If the separation were produced by the sole agency of this agitation, it would appear to us as a miracle, in the sense that the event would be contrary to all scientific anticipations based on Carnot's principle considered as an absolute principle.

But the modern conception of Carnot's principle has exactly the effect of not precluding this miracle; that is to say, in addition to the possibilities which involve physico-chemical evolution towards the most probable states, there is still room for other possibilities; there is room for what are called *fluctuations*.[1]

## 2. *The possibility of fluctuations in living organisms*

But what can be the importance of fluctuations in the interior of a living organism?

[1] For the discussion of fluctuations, see J. de Chim. Phys., *loc. cit.* (or the preceding essay).

The fluctuations which can occur in a given element of volume are, in general, the more important the smaller the number of molecules contained in the homogeneous element of volume considered. *The reply to the foregoing question will depend, therefore, on the degree of tenuity which is attributed to the structure of the tissues and of the living matter.*

But it is known that the structure of protoplasm, which is the simplest form of living matter, is extremely complex. This heterogeneity appears to defy the microscope, since beyond the microsomes, which seem to be the smallest elements perceptible by the microscope, biologists have been led by various hypotheses to assume a still greater heterogeneity, particularly by the hypothesis of micelles, a kind of aggregate of molecules. But all this complexity is localized in the vital element, the cell, the diameter of which does not often exceed a few thousandths of a millimetre.

In other words, the living organism which constitutes the cell can be considered as a sort of mosaic formed by the juxtaposition of a very large number of very small homogeneous elements, and the smaller these elements, the smaller will be the number of molecules which they contain, and the greater will be the importance of fluctuations in the interior of each of them.

Thus it is conceivable that in a sufficiently tenuous homogeneous structure, more tenuous than those which the resolving power of the microscope and of the ultra-microscope enable us to observe, the fluctuations may assume an importance

such that the laws of cellular physico-chemical evolution will no longer be the same as those of our special physical chemistry, in which the fluctuations are almost entirely negligible.

The physical chemistry of the interior of living organisms, which is usually called "physiology," will be, therefore, a more general physical chemistry than that which results from our usual physical and chemical experiments, in which the smallest homogeneous grains of matter with which we operate almost always contain several thousands of millions of molecules, and in which physico-chemical evolution always proceeds practically according to Carnot's principle.

But, it will be said, colloids are very finely divided substances which, nevertheless, obey exact laws. We can ascertain, in fact, their osmotic pressure, measure their velocities of diffusion, and so on; this is incontestable. But the exact laws which we succeed in deriving from these measurements are always collective laws, statistical laws. They do not apply to the evolution of an individual particle, but to a whole which is composed of a large number of particles, and it is only to this whole that Carnot's principle applies, and not to the evolution of each of them. Thus there should be nothing very surprising if Carnot's principle is not applicable to the physico-chemical evolution of an element as heterogeneous as a cell or its constituents. On the other hand, as even the most complex living beings are only the result of cellular proliferation, it is not absurd, by reason of the

extreme heterogeneity of the cell, to suppose that the physico-chemical evolution of living beings at least partially evades the statistical principle of Carnot, in the form which is derived from the physical chemistry of the inanimate world. *For this reason, therefore, the caprice of the fluctuations might be able to play some part in cellular physico-chemical evolution, that is to say, in the development of living beings.*

Let us try, however, to illustrate the foregoing considerations by some figures.

At the present time the number of molecules in a cube the edge of which is a micron in length (0·0001 cm.) can be determined fairly accurately.[1] For molecules of water, to which, for the sake of simplicity, we will assign the formula $H_2O$, this number is about thirty-four thousand million, and it is to be supposed that under these conditions the elementary volume of a micron cube is still not sufficiently small for fluctuations to assume therein, in general, any importance.

But the molecules in organic chemistry, and particularly those which enter into the constitution of albuminous substances, are much more complex; for example, the molecular weight attributed by some chemists to invertin is about 54,000. It is conceivable, therefore, that the number of molecules contained in a micron cube might be approximately 3,000 times smaller, the density being the same,

[1] This number is deduced from the fairly accurate knowledge which we possess at the present time of Avogadro's number.

and this would lead to a number of molecules only of the order of ten millions per micron cube. Under these conditions the possibility of the occurrence of an important fluctuation still does not seem to be very considerable.

But it should not be forgotten that *it would be a very great mistake to compare a cell, the volume of which is several micron cubes, to a homogeneous element*, since we know by microscopic investigations of protoplasm that this substance is heterogeneous. We have seen that in addition to the microsomes which the resolving power of the microscope can reveal to us, biologists have had to advance various hypotheses in order to explain the properties of protoplasm and the functioning of the cell, and in particular the hypothesis of micelles, which pushes the differentiation of living matter far beyond what is revealed to us by the microscope, or even sometimes by the ultra-microscope.

It follows that the elementary volumes which may be considered as homogeneous in a cell are very, very much smaller than the micron cube, and that the number of molecules which each of them may contain is consequently very much smaller than the numbers which we have just cited.

To this consideration is to be added another which is not less important. The heterogeneous fine structure of living matter is not the only factor which may give a particular importance to the statistical fluctuations. At certain *singular*

*points of the physico-chemical evolution* these fluctuations are capable of assuming an exceptional importance. In particular, such is the case, in physics, of the critical point, when the compressibility of a fluid assumes very large values. It results that the least accidental variation of the pressure which occurs in the interior of the fluid gives rise to an enormous change in the density. The fluctuations of the density therefore assume an amplitude which is relatively very great; whence the well-known phenomenon of critical opalescence.

A cube of a micron side in the neighbourhood of the critical point contains approximately one hundred million molecules, and the *mean fluctuation* of the density under these conditions would be about $2\frac{1}{2}$ per cent.,[1] which means that the *individual* fluctuations round the mean density must frequently attain considerable amplitudes.

Thus in the immediate neighbourhood of the critical point a physico-chemical phenomenon escapes from Carnot's principle, in the sense that if an element of fluid, not infinitely small but of the order of magnitude of those which can be studied by means of the microscope, be considered, it becomes impossible to predict from thermodynamical considerations what will be its density at a given instant. In the same way it is impossible to predict from the statistical laws of physical chemistry what would be, at a particular instant, the path of *one* particle agitated by the Brownian movement.

[1] Perrin, *Les Atomes.*

This individual path evades all our physico-chemical previsions, and, in appearance at least, it is not less capricious than that described by any particular bacillus under the microscope. We take care not to say, however, that the particle is living and we had better be reserved in this respect.

The displacements of a particle agitated by the Brownian movement do not appear, in fact, to follow any law, in the sense that it is not possible to deduce the future motion from the actual motion of the particle. It is said that this motion is *not co-ordinated*; it appears to be governed only by the unknown caprice of thermal agitation, and Carnot's principle is only applicable to it with certain reservations. Nevertheless, we do not say, therefore, that the particle is living. In fact, though the motion of the particle does not appear at first sight to be less capricious than that of a bacillus which is observed under the microscope, yet it does not necessarily possess any of the other properties which characterize living matter (the differentiation of its parts, birth, growth, exchanges with the surrounding medium, reproduction, death, and so on). On the contrary, the motion of the particle persists *indefinitely*, so long as the conditions of the fluid in which it is placed remain the same and provided that there are no chemical exchanges between it and the liquid; in particular, it is observed in the liquid inclusions of certain natural crystals which have probably existed for several centuries.

Further, although the Brownian movement may be capricious, it obeys, nevertheless, certain collective laws. If *a very large number of particles* in suspension are considered instead of a single particle, it is found that the mean displacement of these particles is indeed governed by Carnot's principle, and that the physico-chemical laws of diffusion can therefore be again obtained.

But the fact that the Brownian movement is subject to statistical laws is not sufficient to distinguish it from the motion of living beings.

For example, let us consider a large number of bacteria, all having a similar structure, the same mode of nutrition, and of reproduction, and moving approximately in a horizontal plane of liquid corresponding to the hydrostatic pressure which suits them. If we suppose, as it is not absurd to suppose, that the surface explored *on the average* by a bacillus around the position which it occupies is proportional to the time, we shall again obtain exactly the statistical law of the Brownian displacement.[1] A particular statistical law can have various origins; we shall return to this point in our third part. Moreover, do not insurance companies establish statistical laws of mortality at various ages, statistical laws on the number of suicides, and so on, in spite of the complexity of the causes of death? And, as Poincaré has said, these laws are approximately true, since the companies pay dividends.

[1] We have, the surface $\pi r^2 = At$, whence $r$ is proportional to the square root of $t$.

Only a very rare kind of fluctuation would ruin the companies.

In conclusion, whether it be on account of the extreme heterogeneity of living matter, which is favourable to the appearance of fluctuations, or whether it be on account of the possibility, which has been experimentally demonstrated, of the existence of certain singular points at which fluctuations may be exceptionally important, it is not at all absurd to suppose that vital physico-chemical evolution at least partially escapes from Carnot's principle and from its consequences. But when it is stated that the caprice of fluctuations may exercise some effect on cellular evolution, that does not mean that this evolution is not subject to any law. It only means that *the laws of this evolution are no longer necessarily exact statistical laws* as are those of our physical chemistry.[1]

[1] The importance which fluctuations must assume in the interior of a medium which is extremely differentiated strictly permits the consideration of the appearance of life, or even that of hereditary mutations, as the result of very rare fluctuations occurring in the very complex albuminous substances. On account of this complexity there is a prodigious number of different possibilities of action between these substances and the surrounding medium.

Our inability to act on the "individual" fluctuations thus affords a sufficient explanation of our inability to create life from inanimate matter or to produce hereditary mutations. On the other hand, the very rarity of the vital fluctuation justifies the impossibility which we

Moreover, the question of the determinism or the non-determinism of this evolution is not at all decided, of course, by the importance which fluctuations may assume in living matter; it is only transferred into the domain, which is very slightly known experimentally as yet, of the individual actions between molecules, atoms, or electrons.

### 3. *The meaning of physico-chemical laws*

What has just been said about statistical laws and about the possibility of fluctuations, particularly in very heterogeneous media, will allow us to show more exactly, by means of an example, the meaning that the new conception of Carnot's principle appears to us to give to our physico-chemical laws.

In the first place, let us adopt the purely determinist point of view, although we should be more cautious than ever on this fundamental question for the very reason of the new conceptions. For example, let us consider the first 10,000 logarithms in mathematical tables to ten decimals, and let us compile statistics of the frequency of the various figures which occupy the seventh place. It is found

experience of witnessing spontaneous generation, however assiduous our observations may be.

But even if it be supposed that by such considerations we can arrive at an explanation of the genesis of life, this would still be only a slight lifting of the veil. After the appearance of life we have still to explain why this evolution continues, and many other mysteries even to enumerate which would occupy too long.

that the figure 0 appears 990 times ; the figure *one*, 997 times ; the *two*, 993 times ; the *four*, 1,012 times. The law of the appearance of any one of the figures is thus relatively very simple. The relative frequency of each of the figures is very nearly $\frac{1}{10}$. Similarly, the relative frequency of the appearance of even digits is approximately $\frac{1}{2}$.[1]

In this case there are very simple statistical laws which may be compared to the very exact physico-chemical laws which are observed in the inorganic world.

Let us now take the same logarithms in successive blocks of only *one thousand*, and compile the same statistics. The exactness of the statistical law is obscured ; fluctuations appear, as they probably appear when the complexity of the media and their heterogeneity become very great, which seems to be the case in living matter.

[1] We say approximately $\frac{1}{2}$. In a remarkable investigation, Professor Franel, of Zurich, has shown, in fact, that the limit towards which the proportion of the even digits in the $n$th decimal place tends is $\frac{1}{10^{\frac{1}{10^r}}+1} < \frac{1}{2}$ when the number of logarithms considered increases indefinitely in powers of ten. The statistical law is therefore not so simple as it appears at first sight (*Naturforschende Gesellschaft*, Zurich, 1917).

It is more than probable that the apparent simplicity of our physico-chemical laws to a large extent results from the imperfection of our means of observation, and that this simplicity should be subject to reservations of the same type.

Finally, let us consider the statistics for blocks of one hundred logarithms only. The laws of the appearance of the various digits are then entirely different and much less simple than those which result from our first statistics.

For example, here are the frequencies of appearances for the series comprising the first hundred logarithms: *zero*, 20; *one*, 2; *two*, 14; *three*, 6; *four*, 3; *five*, 8; *six*, 11; *seven*, 6; *eight*, 12; *nine*, 18.

In short, we can see that behind the exact statistical laws, behind the incoherence of their fluctuations, there are individual laws. In the example which we have chosen there is the perfectly definite relation which connects the seventh decimal place of the logarithm of a number to the number itself.

### 4. *May we hope to pass from the statistical laws of physical chemistry to the laws of the individual actions between molecules?*

P. Langevin has asked this question and has discussed it[1] from the physicist's point of view, as he should. Moreover, for this he relied on his own researches, which, as is well known, have thrown new and particularly brilliant light on the question of the paramagnetism of gases.

Langevin considers a system possessing a constant energy and introduces the following assump-

[1] La physique du discontinu. Lecture delivered to La Société Française de Physique. *Les progrès de la physique moléculaire.* Gauthier-Villars.

tions: the system contains a very large number of molecules; all these molecules have an identical structure; a statistical equilibrium is established between, on the one hand, the action of an external magnetic field which tends to orient all the molecules in the same direction, and, on the other hand, the action of the thermal agitation, of the precise laws of which we are ignorant; finally, this action of thermal agitation is sufficiently complex to tend to produce all possible orientations.

Starting from these hypotheses, Langevin has been able to calculate what should be the magnetic moment of *one* molecule in order that the experimental laws of the paramagnetism of gases may be satisfied.

Thus he deduces from the observation of a statistical experimental law an individual property of the molecule, its magnetic moment.

In reasoning thus, Langevin, as all physicists should, has set himself the task of explaining in the simplest manner, and only by the conceptions of number, space, time, and matter, the experimental law of the paramagnetism of gases.

But the philosopher is less restricted.

It is not certain, he will say, that the assumptions introduced are the only ones compatible with the experimental law observed. Perhaps it might be possible to arrive at the same result, in a less simple manner, by supposing that some of the molecules have a greater and some a less magnetic moment than the average, and so on. He is entitled to ask whether essentially different individual

laws cannot lead to the same physico-chemical statistical law.

We have seen that by compiling statistics of the figures which occupy the seventh decimal place in the logarithm of a number, we obtain a very simple statistical law, and that this law had its origin in the perfectly definite relation between the seventh decimal place of the logarithm of a number and the number itself. But this same statistical law would have been obtainable from totally different considerations, for example, by supposing that the digits had been drawn by chance from an urn which contained an equal number of all of them, and so on.

Also, to the degree of precision with which we can appreciate the result, it is immaterial whether the figures were drawn at hazard by Tom, Dick, or Harry. In a word, a statistical law can have numerous origins.

In conclusion, it will be seen from the foregoing considerations that the individual laws may be much less simple than the statistical manifestations to which they give rise.

On the determinist hypothesis these laws would correspond to the individual actions which molecules, atoms, or electrons exert on each other.

But it is not at all certain that these individual laws which give rise to the statistical manifestations of our physical chemistry are not essentially more general; there may be something else inherent in them besides the conceptions of number, space, time, and matter which are sufficient for our physico-

chemical explanations. If this point of view be adopted, the essential differences which exist between the phenomena of life and thought, on the one hand, and the relatively simple statistical laws of physics and chemistry, on the other, are less surprising.

### 5. *Conclusions from the second part*

If we consider the problem from the point of view of classical thermodynamics, that is to say, if we regard Carnot's principle as an absolute principle, we find no scientific reason for supposing that this principle is not applicable to the physico-chemical evolution of living organisms.

But since the researches of Gibbs and Boltzmann, Carnot's principle has received a less absolute interpretation; it is considered as a statistical principle which allows us to remain in ignorance of the laws governing the individual actions between atoms, molecules, and electrons.

In addition to those laws of physico-chemical evolution which arise from Carnot's principle, and which only express the most probable evolutions, there is room, in certain particular cases, for other very rare possibilities, namely, fluctuations.

In general, the relative importance of these fluctuations becomes greater as the number of molecules contained in the homogeneous element of volume considered becomes smaller. Further, they may become exceptionally important at certain particular points in the physico-chemical evolution of a system.

Now the fine structure of living matter, which can be conceived to be formed by the juxtaposition of very small homogeneous elements, seems to be particularly favourable to the appearance of fluctuations. Thus we are led to believe that the caprice of fluctuations may very well have some effect on cellular physico-chemical evolution, and even on the development of living beings, if these are considered as the result of cellular proliferation.

The physical chemistry of living beings, which is usually termed physiology, can therefore be considered, from this point of view, as a *more general physical chemistry* than our physical chemistry *in vitro*; in the sense that when it is applied to extremely differentiated media the statistical fluctuations are no longer entirely negligible; they derange the simplicity and the exactness of our physico-chemical laws.

It is remarkable that Helmholtz should have attributed the possibility of a contradiction to Carnot's principle to the *fine structure* of the living tissues at a time *when there was no question of fluctuations.* After some considerations of the motion of heat, and after having recalled that the magnitude of the entropy could be regarded as a measure of the disorder, he expressed himself as follows: "For us, whose methods are coarse with respect to the molecular edifice, only the co-ordinated motion is freely transformable into other forms of energy." And he added as a note: "Whether such a transformation is also impossible in the fine structure of living organic tissues appears

to me to be an open question, the importance of which in the economy of nature is obvious."

It seems that Helmholtz's question is beginning to be answered by fluctuations.[1]

# THIRD PART

## THE PHILOSOPHICAL ASPECT OF THE STATISTICAL CONCEPTION OF CARNOT'S PRINCIPLE

In closing this investigation, we think that a few words on the philosophical aspect of the new conception of Carnot's principle will not be out of place.

### 1. *Determinism or indeterminism?*

Hitherto, the somewhat inevitable finality of the experimental laws of physics and chemistry has constituted the fundamental argument or even the origin and the *raison d'être* of the determinist philosophies.

To-day, the new conception of Carnot's principle teaches us that this finality is not absolute, that the determinism of the laws of physics and chemistry is a larger statistical determinism. Without deciding the question, therefore, it removes the battleground of the philosophical contests between the determinists and the non-determinists into a region which is almost completely beyond our experi-

[1] See the *Supplementary Note*, page 172.

mental control, namely, that of the individual actions between molecules, atoms, and electrons. Furthermore, it shows us that this marvellous precision of the laws of physics and chemistry is only a consequence of what is often called the law of large numbers, applied to individual actions, which may be very complex but the effects of which partially compensate each other when they are very numerous, in such a way as to give the resultant effect a relative simplicity.

But if media which possess a sufficiently fine structure, as is apparently the case with living matter, are considered, the law of large numbers can no longer apply to each of their constituent parts. It can no longer exercise on the resultant effect this compensating and simplifying action which gives the laws of our physical chemistry their apparent simplicity.

The precision of these laws, therefore, must begin to be disturbed and fluctuations will appear. Finally, when the structure is sufficiently tenuous, the true individual laws which are no longer necessarily simple, but which may be even more essentially general than the statistical physico-chemical manifestations to which they give rise, will emerge.

In living matter, therefore, the pseudo-finality of physico-chemical evolution will be capable of modification, sometimes in a direction which at the present time we are not able to predict on account of our ignorance of the intimate nature of these laws and of their hidden individual causes.

In short, behind the exact statistical manifestations which are the experimental laws of our physical chemistry, laws at which we have arrived first by very reason of their relative simplicity, behind the caprice of their fluctuations, are concealed individual laws or the true causes whence these manifestations are derived and whence also seem to proceed life and thought.

If this last point of view be adopted, Carnot's principle may serve as the basis of a philosophic doctrine, which, without at all prejudging the question of determinism, will nevertheless take its place among the *unicist* philosophies. We shall shortly try to outline this philosophy, but before doing so it is necessary to say a few words on the following question.

## 2. *Chance or Finalism?*

Some people have desired to consider chance as the ultimate cause of all evolution, both of the inanimate world and of the organized world of living matter. It has been said that the appearance of living matter is due to the chance of molecular collisions, chance presides at its birth, at its evolution, and at its destruction; "His Majesty Chance," as Frederick II called it when he spoke of its intervention in the fate of battles, asserts itself always and everywhere.

But the word "Chance" has such diverse usages that it is here necessary to define the meaning which is given to it in physico-chemical evolution, by a

few examples. The modern conception of Carnot's principle appears to us to introduce a new element into this important question.

(1) When we have a grey powder composed of grains, some coloured black and some white, it is possible, at least theoretically, to separate them into grains of two colours by shaking them. But it is commonly said to be "the greatest of chances" if this separation is produced by simple agitation; it would be an *extraordinary chance* if, after shaking, all the white grains were to be found in the upper part of the receptacle and all the black grains in the lower part.

In the language of the calculus of probabilities, the fact is stated by saying that the separation of the white and black grains, by agitation, corresponds to *a very rare type of fluctuation.*

Similarly, in a uniform mixture of two gases, it would be an extraordinary chance if at a given moment, and solely by the action of thermal agitation, all the molecules of one gas were at the right of the receptacle and all those of the other gas were at the left. In reality, this configuration might perhaps be neither more nor less probable than any other predetermined configuration, but *it would confer on the system properties different* from those which are possessed by configurations which are infinitely more numerous, corresponding to what we call an approximately uniform mixture. For example, the fluctuation which results in all the white grains being in the upper part and all the black grains in the lower part of the receptacle produces

a different impression on our eyes from that which is produced by the innumerable configurations which correspond to the grey powder. But these different properties permit us to distinguish these fluctuations ; they authorize us to consider them sometimes as the result of what we have called an extraordinary chance.

Let us consider now a uniform mixture of the gases $CO_2$, $H_2O$, $N_2$, and some other elements, which are the constituents of living matter. Let us suppose this mixture to be first of all sterilized by a high temperature and then subjected—for example, through a quartz window which transmits the ultra-violet rays—to the action of the light from the sun, not for a few days or years, but for an immense number of centuries. We should be able to assume then that all the dissociations, combinations, and associations of atoms, molecules, and electrons which can be produced by the action of light and thermal agitation, in a word, all the effects which are *possible*, will be realized in the course of the ages.

Thus a molecular association corresponding to the physico-chemical constitution of living matter would be produced at some place in the volume.

From this hypothesis the appearance of life would be due, therefore, to a *fluctuation of a very rare type* ; that is to say to what we commonly call an extraordinary chance.

Let us observe, however, that if we are allowed to make this assumption, it is because we know next to nothing concerning the passage from non-living matter to living matter. All that we know

definitely is that, on the one hand, we have never been able to produce it in our reactions *in vitro*, and on the other hand, that we have never been witnesses and spectators of such a transformation; these are two conditions compatible with the hypothesis of a "very rare" fluctuation.

But if, rigorously and for the reasons just given, we can compare life to a very rare fluctuation, this is no longer the case if we endeavour to explain the physico-chemical evolution in the interior of a living organism.

In fact, when the task of constructing a predetermined edifice is committed to an extraordinary chance, this singular constructor, who in general is never in a hurry, must be given time to build numerous unfruitful configurations until the desired configuration emerges.

But this lost time is not observed in the physico-chemical evolution of an organism. We may conceive that the chance of molecular collisions might *once* have constructed an optical instrument in the interior of a living being,[1] but it is more difficult to suppose this to be done at the first attempt, not only in the organism considered, but again in all the living beings which constitute its progeny.

Thus the success of the construction cannot be

[1] We have chosen the construction of an eye in the interior of a living organism as an example of vital physico-chemical evolution because this example is particularly calculated to appeal to a physicist; but numerous examples are to be found in biology in which the real or apparent finalism of vital evolution is equally manifest.

attributed to an uninterrupted series of extraordinary chances; to some extent that would involve at each instant a miracle analogous to that which M. Emile Borel, in his book on chance, calls "the miracle of the typewriting monkeys."[1] We must therefore discard immediately such an improbable hypothesis.

(2) But though vital evolution cannot be considered as an uninterrupted series of extraordinary chances, nevertheless it can be considered as a consequence of what may be called *the laws of chance.*

In order to define more clearly the meaning which must be attributed to this term let us return to Carnot's principle, and, contrary to the conclusion reached in our second part, let us for a moment admit this principle without any reservations, that is, let us neglect the fluctuations in both the organized world of living matter and in the inanimate world. It follows that at each instant of the vital evolution, this evolution will proceed towards the most probable of all possible disorders. (See second part.)

But then it becomes necessary to suppose that at each instant there are *new possibilities* which are to some extent dependent on the actual state and which determine the most probable immediate

[1] Let us suppose, says M. Borel in so many words, that we have set a million monkeys to hit the keys of a million typewriters. How many thousand million centuries would have to elapse in order that, if the manuscripts were collected periodically, it would be found that this blind activity had produced exactly all the volumes which actually exist in the library of the British Museum?

evolution and so on. Otherwise, as has been said, in order to explain this evolution which is always going on we should have to assume a miracle analogous to the miracle of the typewriting monkeys.

But these new possibilities which are dependent on the actual state are essentially only a disguised finalism. For instance, in the example which we have chosen, why should these possibilities, which characterize each actual state, be always such that the most probable evolution proceeds exactly in the direction of the *continuation* of the construction of the optical instrument ? The finalism which was thought to have left by the door has actually come back through the window. It has been gratuitously reintroduced in the conditions which determine, at each instant, the new possibilities of evolution.

(3) Finally, if the point of view developed in our second part be adopted ; if the statistical principle of Carnot is not absolute, on account of the extreme division of living matter, we shall still be confronted with the same question. How is it that the vital physico-chemical evolution towards the most probable states, this time profoundly altered by the importance which is assumed by fluctuations—how is it that this evolution always proceeds in the direction of the *continuation* of the construction of the optical instrument ?

Thus it is apparent that the invocation of the laws of chance is not sufficient to banish all finalism from the vital evolution. On the contrary, it seems that it must be given a certain place, in one form or another, whether it be called finalism, tendency,

vital spark, soul, principal organizer, or anything else.

Now this element which, rather vaguely, has here been called finalism, has been introduced in various ways by philosophies and religions.

Some of them, the *dualist philosophies*, consider it to be an element in some way exterior to what we have called matter. Confronted with the difficulty of conciliating the determinist laws of the ordinary physico-chemical evolution with the manifestations of life and conscious thought, their exponents have preferred to divide the problem into two.

The statistical conception of Carnot's principle also permits such a subdivision. In fact, it is possible to conceive the laws between molecules, atoms, and electrons as being perfectly definite, but to assume the intervention in living organisms of a kind of Maxwell's demon which is to some extent capable of directing their course. This hypothesis has already been mentioned in our second part.

Other philosophies, *monist or unicist philosophies*, remember above all the experimental fact that life and thought are always associated with what is usually called matter; they endeavour, therefore, to get back to a unique explanation of everything. But then, not being able to deny the determinism of physical and chemical laws, they voluntarily extend this determinism to all the phenomena which accompany life.

The new conception of Carnot's principle also allows a unicist philosophy; but this conception is

larger. It is no longer necessarily determinist since it is able to localize the origin of life and conscious thought in the individual actions between molecules, atoms, or electrons; the determinism of physics and chemistry only being a statistical determinism, the accuracy of which is only due to the law of large numbers.

In conclusion we shall consider the question from this last point of view, which appears to us to call for further explanation.

### 3. *Outline of a unicist philosophy based on Carnot's principle*

According to the principle of relativity, what are called the constituent elements of matter (molecules, atoms, electrons) are only energies, of the intimate nature of which we know nothing. These elementary energies are of different kinds, to the number of about 80, the atoms of simple substances. But the recent discoveries of radioactivity and of isotopes, and modern researches on X-rays, tend to reduce the number of these elementary energies to two: *the negative electron and the positive electron.*

By suitable groupings of these energies, not only do they give rise to what we call physico-chemical phenomena but also to the manifestations of life and thought which sometimes accompany them. Thus it appears natural to assume that these energies cannot be defined entirely by the conceptions of number, space, time, and matter which suffice for

our physico-chemical explanations; they must inherently involve *some other conception.*

We say that these elementary energies attract or repel one another, or, if we prefer to use a more finalist language, they seek each other or fly from each other in such a way as to build up structures possessing certain characteristics of dissymmetry which permit them to act on the chaos of unorganized energies and to realize thus the possibilities which are inherent in them. As Curie has remarked, a phenomenon can only occur or even be propagated if a dissymmetry exists. We shall suppose, therefore, that the first tendency of these energies is to create dissymmetrical structures which confer on them the power of acting on the medium which surrounds them.

But in the forefront of the energies most suited to the formation of these powerful dissymmetrical structures are those we call the atoms of carbon (*tetravalent*) and nitrogen (*trivalent*) associated with atoms of hydrogen and oxygen; all of these are elements which are extremely numerous on the surface of our earth. These associations thus form the principal basis of the albuminous substances, which are well known to be remarkable for their extreme complexity. On account of this very complexity, therefore, they can produce an almost infinite variety [1] of phenomena, and thus realize the possibilities which are inherent in them.

[1] By means of the laws of permutations an approximate idea can be formed of the prodigious way in which the possibilities of isomers increase when the number of atoms

With the help of Carnot's principle, let us now try to define what distinguishes, schematically, a physico-chemical phenomenon from a vital phenomenon, although on a unicist theory these two phenomena are always more or less associated with each other.[1]

Let us consider a medium of definite extent which we shall suppose to be homogeneous and isotropic. For example, a sphere of oil in suspension in a mixture of water and alcohol of the same density. We shall suppose that *this sphere is screened from all exterior dissymmetrical forces capable of altering its homogeneity or its isotropy in an appreciable manner.*

Under these conditions *the statistical resultant of the interior forces will be negligible, for reasons of symmetry,* at every point in the inside of the sphere

in the molecule is increased. If the albumen molecule contains, for example, a thousand atoms and if these atoms could arrange themselves in the course of ages in all possible ways, which is not at all certain, they would give rise to $1 \times 2 \times 3 \ldots \times 1{,}000 = 1{,}000!$ permutations. It is useless to try to represent such a number. It is sufficient to recall that a hostess can arrange twenty diners round a table in more than two million million million different ways. What would it be if it were necessary to place one thousand ? It is true, however, that these innumerable isomers would not all constitute varieties of albumen. Stereochemistry shows that beyond doubt many would be stereochemically equivalent. Nevertheless, in spite of these restrictions, there is still a very large margin of possibilities.

[1] We do not think that this has been done accurately hitherto.

which is not very near to the surface ; these forces, therefore, can only give rise to a symmetrical internal pressure, and this is exactly what is observed in homogeneous fluids.

On the contrary, at the surface of separation of the sphere the dissymmetry will give rise to forces. If the element of surface considered, though small, nevertheless contains a very large number of molecules, these forces can be considered as *statistical surface forces.* They are called, therefore, surface tensions, contact electromotive forces resulting from double layers, and so on.

These forces which are due to dissymmetry at the surface of separation of two different media are essentially those which must be considered as the true causes of the production of the physico-chemical phenomena which we study in the inanimate world. In the ultimate analysis these are the forces which, in conjunction with the mysterious weightiness (gravitational field), form the origin of physico-chemical evolution in conformity with Carnot's principle.

Let us take the preceding example and let us suppose that the sphere of oil, instead of being in equilibrium in a liquid mass which acts symmetrically on it at every point, is situated at the surface of the water. The resultant of the statistical interior forces will remain practically nil at every point inside the sphere, but the surface statistical actions will have an action on account of the dissymmetry created. The oil, under the action of the surface tension, will spread over the surface of the

water, liberating energy. In short, everything will take place according to the ordinary laws of our physical chemistry and in conformity with Carnot's principle, so long as the film of oil contains a large enough number of molecules per unit area for the *statistical* conception of surface tension to persist.

This will also be the case for spheres of very small volume, since it is known that a micron cube still contains approximately thirty thousand million molecules. Matter may therefore be in a very finely divided state and yet obey Carnot's principle.

But suppose that this division is pushed to extremes ; let us assume that the mass of the sphere, like that of a micelle, no longer contains more than a relatively small number of molecules ; fluctuations will appear both in the case of the interior actions and that of the surface actions. *The statistical resultant of the interior forces will no longer necessarily be nil and the precision of the surface actions will also be altered by the fluctuations.*

At length, when the division is sufficiently fine, the intimate nature of the individual laws will become manifest. On our hypothesis it is then that life, with its phenomena of sensibility and conscious thought, can make its appearance in an appreciable manner.[1]

[1] In this connection it is important to observe that life, in order to manifest itself to an appreciable extent, demands the co-operation *of a very large number of free molecules* ; in other words, the living matter, the protoplasm, always contains liquids in abundance. Also, life

In conclusion, so long as the elementary energies constitute uniform fluid mixtures of sufficiently large volume, their individual powers of action will compensate and will practically neutralize each other ; life exists, but in the latent state, without the possibility of manifesting itself ; it is the internal statistical pressure in the midst of a homogeneous fluid, and only by a sufficiently fine differentiation and organization can these elementary energies succeed in assuming all their power

does not appear to have originated from the solid part of the earth's surface ; on the contrary, paleontology teaches us that the first living organisms were born in the bosom of the oceans, those inexhaustible reservoirs of free molecules, and that it was not till later that they emigrated to the islands and continents. It is true that certain organisms can support a long drought with impunity, but the activity of their life is then as it were suspended ; if replaced in a humid medium they can reassume life if the dissymmetrical structures which characterize life have not been destroyed. Similarly, when certain organisms (bacteria, for example) are subjected to a low temperature, if this cooling has not produced dislocations and alterations of such a nature as to compromise their functioning, they reassume life when they are raised to a higher temperature. In particular such is the case with certain phosphorescent bacteria which, it is said, can survive unharmed a week at the temperature of liquid hydrogen (— 253°).

On the contrary living matter is irrevocably destroyed by the energetic shaking up due to the thermal agitation which corresponds to a temperature of between 100° and 200° C. On our hypothesis a relatively short time at such temperatures is sufficient to destroy the dissymmetries which give living matter its inherent power to act on the surrounding medium.

to act on the chaos of the non-organized energies which surround them.

But in so far as this complication, this dissymmetry, increases, the power of action of living matter becomes greater. It then becomes easier for it to realize the possibilities which are inherent in it. Its finalism increasingly asserts itself; it becomes more manifest, and the curious phenomena of adaptation and of sensibility, which seem to be revealed like a hidden intelligence, are seen to appear more clearly.

We can proceed still further with this outline, always, it is true, getting farther away from our starting-point, the statistical laws of physics and chemistry. What our outline will gain in extent it will lose in accuracy; this is the inevitable law of all philosophical extrapolation.

This dissymmetry, which creates its power, is felt by living matter to be very frail. It is unceasingly menaced and exposed to destruction by the chance of external forces and particularly by that terrible *shaking up* which is called thermal agitation, and which is the grand enemy of all dissymmetry. Also, the first care of living matter is to assure the continuity of its action in order to conserve the possibility of realizing itself more completely. With this object in view it creates most frequently, sheltered from exterior conditions, in the embryo or in the egg, a very dissymmetrical structure, similar to itself, but one which it does not put into contact with the exterior medium until its differentiation is sufficiently developed to

allow it to struggle successfully against the external forces which tend to destroy it. The maternal instinct sometimes even continues to protect it at its commencement of the struggle. At the same time physical and moral joy and suffering serve to direct the course of its evolution.

But these energies which endeavour to realize themselves in living organisms also enter into conflict with each other without delay. It is then that there arise for these organisms, at first in a more or less rudimentary form, the moral problems of good and evil, of egoism, of altruism, of solidarity and so on.

On the other hand the continually renewed spectacle of the physical and moral sufferings which result from these conflicts and from the struggle against the chaos of non-organized energies, remains particularly perplexing. In order to explain them, philosophical and religious doctrines then make their appearance, at the same time endeavouring to guide the human ideal in conformity with what are otherwise very diverse tendencies.

Of these tendencies we shall only consider two, because they are to some extent in opposition to each other.

To the philosophers of India, struck by the eternal return of events, the appearance of life must be regarded as an unfortunate accident, the source of innumerable sufferings. It is therefore necessary to desire that eventually the chaos of statistical phenomena shall end by reabsorbing it; life and conscience will then be annihilated in the *nirwana*.

Such a philosophy can be considered as the expression of the pessimism and the discouragement inherent in a civilization which is more or less crystallized and the evolution of which is actually paralysed.

But a civilization in the process of evolution and of progress would be right in adopting a diametrically opposite point of view and in supposing that in its evolution life will always succeed in producing superior organizations ; that these powerful organisms will end by dominating completely the chaos of physico-chemical phenomena ; that they will perhaps succeed in vanquishing even death, which, from the point of view that we have adopted, is only the triumph of the chaos of non-organized energies over organized energies ; and that finally, guided by a superior morality, these organisms will ultimately attain happiness, the final goal towards which appear to be directed the more or less conscious or unconscious efforts of individuals or societies.

But here we are very far from our starting-point, which can be summarized essentially as follows :

*The physico-chemical evolution governed by Carnot's principle is due to statistical actions, but the cause and the origin of the organization of life and thought must be sought in individual actions.*

Such is the point of view which we have endeavoured to cause to emerge from the present ideas, without concealing from ourselves, however, the difficulties, the objections, which may arise in its development, and which arise moreover in all

philosophical doctrines. Nevertheless, we have persisted in outlining it in order to demonstrate, by means of an example, the *powerful philosophical fertility* of the new statistical conception of Carnot's principle.

We ask the reader to be good enough to pardon us for having sometimes carried him, perhaps in spite of himself, right into the realms of metaphysics.

## SUPPLEMENTARY NOTE

The idea that Carnot's principle might not be rigorously applicable to the physico-chemical functioning of living organisms is not at all new. We were under the impression that H. Helmholtz was the first to propound it. (*Die Thermodynamik chemischer Vorgänge*, aus Sitzungsberichte der Akad. der Wissenschaften zu Berlin, r. 2, II, 1882.—Helmholtz Abhandlungen, II, p. 972.)

Daniel Berthelot has been good enough to draw our attention to the fact that Sir William Thomson (Lord Kelvin) had previously advanced the same idea in the following form : " It is impossible by means of *inanimate* [1] material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of surrounding objects." (W. Thomson, *Dynamical Theory of Heat*, § 12, 1852.—*On a universal Tendency in Nature to the Dissipation of Mechanical Energy*, Proceedings of the Royal Society of Edinburgh, April 19, 1852.)

In this statement, which he considered as axiomatic, Sir W. Thomson was therefore already making reservations on the generalization of Carnot's principle to the physico-chemical functioning of living organisms, thirty years before the remark of Helmholtz, which, it is true, was more explicit, involving the fine structure of the living tissues.

The probable importance which fluctuations must assume in matter which is as heterogeneous as living matter, has appeared to us, whilst considering it, to endow this question with an entirely new interest, and to merit the developments which have been given it in our third essay.

[1] The italics are ours.

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